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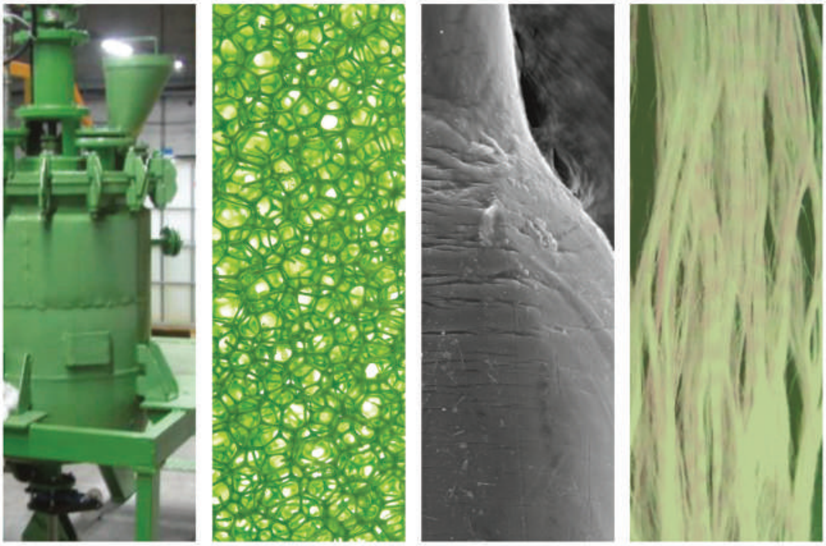

Victor A. Goldade and Nataly S. Vinidiktova

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Contents

Preface

Since ancient times, the mankind uses fibrous materials for production of clothes, tools, as well as for medical purposes. For example, the use of fibers in medicine was first mentioned in *Surgical Papyrus*, nearly 4000 years ago. In the Indian manuscript *Susanta Sambita*, written approximately 2500 years ago, a variety of fibrous materials are mentioned such as horse hair, leather strips, cotton, animal sinews, and fibrous tree bark. At present, textiles have found their way into a variety of medical applications. In addition to protective medical clothing, textiles in the form of fibers and fabrics are used as implants, filters, and surgical dressings. Recent decades have witnessed major development in the production of medical textiles, as well as in materials and technologies used to manufacture them.

The global problem of technogenic deterioration of environmental conditions for life on Earth have been considerably aggravated in the 21st century. The problems of local reduction of detrimental effects of the changed environment on human beings and the sphere of their existence have become topical as never before.

In the system "human—textile product—habitat," the textiles act as protection for a person. The new generation textile products which are produced taking into account the adverse changes in the ecological environment are actively minimizing their effect. Additional functional properties are being imparted to polyester fibers which are traditionally incorporated into the composition of practically all textile fabrics to increase their wear- and crease-resistance. The best world samples of polyester fibers possess antimicrobial activity and an ability to discharge static electricity, demonstrate the reduced combustibility, and have other special properties. American, Chinese, Japanese, and other textile products have appeared in the market which react "smartly" to the change in environmental parameters, reducing its harmful effects on a human being. Targetedly modified polyester fibers are an indispensable component of such products.

Chemical fibers are obtained from products of chemical processing of natural polymers (artificial fibers) or from synthetic polymers (synthetic fibers). Despite continuous improvement of the textile production and advancement in technologies for chemical fibers, not many methods to impart them with special properties are developed. Classical methods for filling and plasticization of the polymer base have long remained a sole instrument to regulate the chemical fiber properties. Currently, the targeted modification of the surface layer of fibers which does not affect their core has become the leading trend in the textile materials science. Such modification is implemented predominantly by the diffusion mechanism using the technological environments which are thermodynamically compatible with the polymer base of the fibers. The latter condition is a significant limitation to the range of technological impact on the structure of the surface layer, thus making it impossible to introduce a lot of very effective target modifiers into it.

As an alternative, production of multilayer fibers consisting of polymer core (which properties essentially determine the deformation-strength characteristics of the fiber) and one-two external layers which impart the fiber with special properties (wettability/nonwettability, frictionality/antifrictionality, high fusibility/low fusibility, etc.) has experienced active growth in many countries in the 1990s. However, interest in them quickly faded due to high costs of the considerably sophisticated industrial equipment, low stability of technological process of extrusion “facing” of the fibers, unreliability of multitubular extrusion heads and complexity of their repair.

The situation was radically changed at the introduction of the methodology of surface modification of chemical fibers based on implementation of the crazing phenomenon. Crazing is a process of plastic deformation of polymers which brings them into a specific structural state. At loading levels and properties of the environment (which are individual for each material), special areas of the oriented state—crazes—occur in the specimen. These are microcracks which walls are connected by fibrils less than 10 nm in diameter. Crazing was first discovered and studied by the American physicist-chemists E.I. Kramer, R.P. Kambour, A.S. Argon, and M.M. Salama; their first publications on crazing were issued in the early 1970s. The extent of crazes opening in the polyester fibers (in glassy state at room temperature) subjected to orientational drawing in the surface-active liquid media which promote cracking of fibers provides for the possibility to introduce into the surface layer of the fiber any substances, irrespective of their physico-chemical nature.

The extremely slow (months, years) release of the nonvolatile substances captured in the crazes to the environment which was discovered by Russian scientists N.F. Bakeev and A.L. Volynskii is of equal practical interest. At first, crazing was used in the processes of water-repellent fibers dyeing, and in the 1980s–1990s to produce semiconductor and low-combustible chemical fibers.

Nevertheless, crazing has not found application yet in large-scale production of chemical fibers and is very seldom used in the technology for their processing. As a rule, basic methods for chemical fibers modification by the mechanism of crazing are the know-how of the leading manufacturers of fibers with special properties which are closed to third-party experts.

This book summarizes the data available in scientific and patent literature on physico-chemical nature of crazing and discusses the results of original researches performed by the authors on implementation of this phenomenon at drawing the synthetic fibers which resulted in development of new technologies to produce multifunctional fibers.

The research findings presented in this monograph are obtained with financial support from the scientific and technical program “Composite” of the Union State of Russia and Belarus and are complemented with the results of activities performed under the contract with UNIKO Chemical Co., Ltd (South Korea) and the researches conducted by an order of the state program of scientific researches “Functional Materials” of the National Academy of Sciences of Belarus.

The authors would like to express their gratitude to Sergey Zotov, Elena Klimovich, and Tatyana and Konstantin Ovchinnikov, employees of the Metal-Polymer Research

Institute of National Academy of Sciences of Belarus, for their creative participation in carrying out the experiments, including the ones on the industrial equipment, the results of which are presented in the book. We dedicate this book to the memory of our untimely deceased friend, colleague, and teacher, Professor Leonid Pinchuk, whose ideas are implemented in a number of our joint publications and inventions.

Victor A. Goldade and Nataly S. Vinidiktova

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Abbreviations and denotations

AFM	atomic-force microscopy
AL	artificial leather
BF	bicomponent fibers
CRA	coefficient of repellent action
DDT	dichloro-diphenyl-trichloromethylmethane
DETA	diethyl toluamide
DMP	dimethyl phthalate
DNA	deoxyribonucleic acid
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EMR	electromagnetic radiation
EO	essential oil
EPA	Environmental Protection Agency
MPC	maximum permissible concentration
OI	oxygen index
PA	polyamide
PAN	polyacrylonitrile
PBDE	polybrominated diphenyl ethers
PET	polyethylene terephthalate
PP	polypropylene
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
RAM	radioabsorbing materials
SAS	surface-active substance
SEM	scanning electron microscopy
SS	Seignette salt
Tr	triclosan
$\boldsymbol{T}$	temperature
$\boldsymbol{T}_b$	boiling temperature
$\boldsymbol{T}_{br}$	brittleness temperature
$\boldsymbol{T}_g$	glass-transition temperature
$\boldsymbol{T}_m$	melting temperature
$\boldsymbol{T}_y$	yield temperature
$\boldsymbol{\varepsilon}$	relative elongation
$\boldsymbol{\varepsilon}^*$	draw ratio
$\boldsymbol{\sigma}$	stress; specific conductivity
$\boldsymbol{\sigma}_{br}$	breaking point
$\boldsymbol{\sigma}_y$	yield point

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Polymer restructuring at plastic deformation

1

The process of plastic deformation of solid polymers, which is well studied and described in numerous encyclopedic and reference books, takes place by physical and chemical mechanisms which are not similar at different stages of deformation. Since, in most cases, the final result of deformation is of primary importance, its intermediate stages and the corresponding polymer restructuring are therefore often neglected.

Let us take the following example. At drawing a polymer specimen up to the yield point (the Hookean region in the stress-strain curve), the elastic deformations are evenly distributed throughout the specimen volume. After the yield point has been reached (the curve area from the yield point to the point where the constant value of stress in the specimen is reached), the distribution of deformations becomes uneven. Areas with different extents of deformation divided according to the so-called shear bands are formed in the specimen. This means that the polymer material structure has lost its stability in the mechanical stress field. Appearance of the yield "drop" on the stress-strain curve is a sign of loss in stability. A neck is formed in the specimen, followed by a period of forced yielding when orientation of supramolecular formations and free macromolecules along the axis of tension takes places. The multistage transition to the flow is another type of the loss in structural stability by the material.

Most often, only materials scientists pay attention to such details, since the designers and technologists are interested primarily in integral indicators of strength and deformation of polymer material. However, the processes of loss in stability are of great practical interest as the basis for development of methods to modify the polymers with substances which are thermodynamically incompatible with them. Physico-chemical mechanisms of loss in stability (which are called "the self-organization phenomenon in polymers at deformation" in Ref. [1]) are discussed later. They constitute the scientific basis for technologies of target modification of chemical fibers covered in the book.

1.1 Terminology

At first glance, it seems superfluous to pay attention to basic terms of physics and materials science of polymers as their definitions can be found in encyclopedic publications. However, analysis of the works on physical chemistry of polymers shows that numerous nuances related to establishment of new patterns in polymer materials deformation have emerged in interpretation of these terms in recent decades. In addition, many similar terms, often buzzwords, taken from the translated literature with a close but slightly different meaning have appeared.

When presenting the book material, the authors seek to give the most correct description of physical and chemical mechanisms of the polymer structure transformation in the process of deformation. The reliability of scientific rationales for new

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industrial technologies described in this book depends, to a great extent, on the accuracy of such assessments. We believe that the refined interpretation of the terms given below will allow us to present more convincingly the physico-chemical background for new technologies.

The *crystalline state* is energetically the most favorable condition of the substance, therefore the natural change in time of the structure of solid bodies inevitably brings them to varying degrees of orderliness.

In principle, synthetic polymers consisting of flexible macromolecules of various lengths (molecular-weight distribution is one of the most important characteristics of their structure) cannot be completely crystalline. Crystallization occurs by the mechanism of chain folding at nanodimensional areas, thus leading to formation of crystallites which form the crystal phase registered by X-ray diffraction techniques. The chains that have not been incorporated into the crystallite constitute the adjacent amorphous phase.

The thermodynamic impossibility to obtain 100% crystallinity of synthetic polymers was a reason behind naming the polymers capable of crystallization as “partially crystalline” or “amorphous-crystalline.” This stipulates, firstly, the availability of significant free volume in their structure and, secondly, the potential possibility to fill it with target modifiers; this fact was first noted by the outstanding Lithuanian physicist-chemist and materials scientist A.N. Machulis [2].

The *high-elasticity state* is a physical condition of polymer materials in which they are capable of huge (about hundreds of percent) reversible deformations at strain. Unlike inorganic crystals which deformation is accompanied by the change of interatomic and intermolecular distances, high-elastic deformation of polymers is related to expansion of flexible macromolecules and movement of their links. The force that returns the chains into the initial position does not result from intermolecular interactions, but is generated by thermal motion of links. At thermal motion, flexible macromolecules can be in different conformations; these are possible due to availability of free volume in the polymer structure. Conformational transition occurs at rotation of the chain links around individual bonds and is accompanied by the changes in free energy $W=U-TS$ and entropy S, while the internal energy of macromolecule is $U=\text{const}$.

Forced high elasticity, which has recently been named “shear yielding,” develops in the process of deformation of polymer specimens under stresses exceeding the yield point. It is a piece of the polymer material flow on the stress-strain curve.

The *glassy state* is the nonequilibrium state of the solid substance which occurs at hardening of its overcooled melt. When heated, the substances in the glassy state are softened and change into the high-elasticity state. Reversibility of this transition at the temperature decrease is a feature which distinguishes the glassy state from the other noncrystalline states. The emergence of the glassy state is accompanied with the decrease in the substance internal energy. The crystalline state is a steady-state condition corresponding to the absolute minimum of energy. Therefore, materials in the glassy state are metastable, and their structure is becoming ordered in the course of time.

High-molecular compounds belong to the class of substances which can go into the glassy state. This develops in polymers with primary irregularity of molecular structure: irregular sequence of monomer units in a macromolecule [polystyrene, polypropylene (PP), polyethylene terephthalate (PET)] and branching in macromolecules. Flexibility of macromolecules decreases as the melt of such polymers cools down. This interferes with arrangement of the macromolecule segments into crystallites, and deep supercooling of the melt results in “freezing” of the short-range order in the chain links arrangement. The number of conformational states of macromolecules reduces and, respectively, the entropy of fusion drops dramatically or vanishes. The loss in yielding flow and high-elastic deformation capability by the polymer material stipulates a transition to the glassy state.

At temperatures below the melting temperature ($T<T_m$), three relaxation transitions γ, β, and α (designated according to the temperature increase) take place in the amorphous-crystalline polymers. The α-transition is usually associated with the mobility of segments in crystallites; the β-transition—with the mobility of large segments and γ-transition—small segments in noncrystalline areas. When heated, polymer glass acquires high elasticity, unlike the low-molecular glassy substances, which melt upon heating.

The *amorphous state* is the solid noncrystalline state of the substance which is characterized by isotropy of physical properties, lack of melting point, and ability of some substances to crystallize when heated. The latter feature has been included in the definition of amorphous state owing to the works of Russian physicists A.I. Popov [3] and V.S. Minaev [4] who studied the thin noncrystalline films. Unless this feature is taken into account, the notions of “amorphous” and “glassy” states turn out to be identical. Therefore, there is a common feeling that the notions of amorphous and noncrystalline states of the substance are identical; this opinion is expressed in a number of encyclopedic and reference books.

Let us take the following examples. In the *Encyclopedia of Polymers*, it is stated that “amorphous polymer materials can exist in three physical states – glassy, high-elastic and viscous-flow ones” [5]. In the *Encyclopedia of Physics*, it is written that “the glassy state is the amorphous state of the substance which is formed at hardening of the supercooled melt” [6]. P.P. Kobeko, a classic of the Soviet physics, has given the following definition in Ref. [7]: “The substances which do not have crystalline structure are called the amorphous bodies.” The same confusion between the notions is also characteristic for [1]. Therefore, a cautious assessment of the nature of amorphous state in the *Chemical Encyclopedia* is not surprising: “the issue of thermodynamic nature of equilibrium solid amorphous state remains open so far” [8].

Examples of amorphous substances include tetrahedral semiconductors of germanium and silicon, as well as red selenium which retain their amorphous state in isothermal conditions for a long time, but are crystallizing at temperatures above critical [9].

The structure of amorphous polymers is characterized by the short-range order in arrangement of the macromolecule units which is quickly disappearing as the distance between them grows. Long molecular chains can be formed into bundles which have a very long lifetime because of the huge viscosity of polymers [10]. The unordered phase of crystallizing polymers occurs in the amorphous state. This is evidenced by the phenomenon of secondary crystallization, which starts after the primary crystallization of the melt has occurred. It complies with the improvement of order in the formed supramolecular structures and in noncrystalline phase of macromolecules at temperatures above the glass-transition temperature [11].

Temperature ranges of the polymer physical states are divided by the characteristic intervals of temperatures and not by temperature points. The reason for this is the existence of molecular-weight distribution of synthetic polymers and availability in the structure of solid polymer material of several differently ordered phases. In low-temperature range (~10 to 30°C) the noncrystallizable polymers or the ones which have not been timely crystallized become solid, i.e., they go into the glassy state. This interval is conventionally characterized by the glass-transition temperature T_g. The brittleness temperature T_{br} (at this temperature the polymer material displays brittleness in the process of loading) is below it. However, the latter is not considered as a constant of the material, since T_b value depends on the rate of loading.

Above T_g, the amorphous polymers are in high-elastic state. Its upper limit is determined by the yield temperature T_y. At this temperature, the polymer changes (under heating) from the high-elastic state into the viscous-flow one. For glassy polymers with a low molecular weight, T_y practically matches T_g, while for crystallizing polymers the melting temperature is T_m. The latter characterizes the temperature range (sometimes up to tens of degree Celsius) in which the polymers acquire viscous-flow property. External effects disturbing the statistical balance of the macromolecular structure generate the relaxation phenomena which change temperature limits of the polymer physical conditions.

Shear bands are a specific form of development of inelastic deformations in glassy and crystallizing polymers. The system of rectilinear cracks of about 1 mcm wide is formed in the specimen when subjected to loading after the proportionality limit has been reached. Microcracks which are visible under the optical microscope intersect the specimen at an angle of 45–55 degree to the axis of tension (Fig. 1.1). Their occurrence

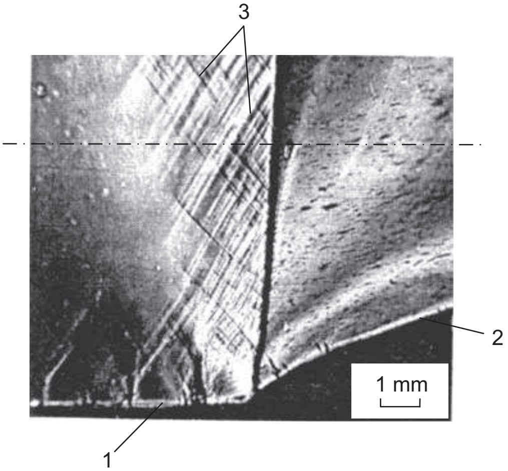

Fig. 1.1 Surface of PET specimen deformed at $T = 20°C$ with neck formation. 1—initial area, 2—neck, 3—shear bands; the axis of tension is shown with a dash-and-dot line. Reproduced from Volynskii AL, Kechek'yan AS, Grokhovskaya TE, et al. On the mechanism of deformation of polymer glasses. Polym Sci Ser A 2002;44(4):615–28 with permission from Pleiades Publ., Ltd.

is an evidence of uneven distribution of deformations, and the shear bands themselves are a place of their localization [12]. They divide the blocks of nondeformed polymer with the initial unchanged structure. When subjected to loading, the blocks slide along the shear bands, causing the forced high elasticity of the polymer. This process, which forms the core of the polymer materials orientational drawing, is accompanied by accumulation of significant amount of internal energy in the shear bands [13]. The effect of the energy accumulation is experimentally confirmed by the enthalpy growth in the deformed polymer detected by DSC method [14] and is directly registered by special methods of calorimetry [15].

The *neck* is a local narrowing of a solid polymer specimen at uniaxial drawing. The neck is initiated at the moment when tension extends beyond the yield point. The material which passes into the neck is permeated with shear bands (Fig. 1.1) and undergoes (in the neck) irreversible processes of loss in structural stability. These processes for the flow of polymer in the forced elasticity state and its transition into the oriented state. Cross-section areas of the initial and narrowed (as a result of neck formation) parts of the specimen do not change at flowing.

The flow process may become nonsteady and occur in the self-oscillation mode (Fig. 1.2) when the tension, rate of the polymer structural transformations, and the specimen temperature are periodically changing [16]. Deformation self-oscillations determine the variable mode of heat exchange between the specimen (which is warmed up due to adiabatic transition of the deformation activity into the heat) and the environment. As a result, the oriented-in-the-neck specimen acquires a regular structure which is visible under the microscope as alternating dark and bright lines.

The nonequilibrium process of the neck formation occurs by the relaxation mechanism and takes place with continuous consumption of mechanical energy.

Fibril is a thread-like structure consisting of crystallites and/or molecular chains oriented along the thread axis. This term was first proposed in biology to refer to the mechanical-load-bearing thread-like protein aggregates in the animal cells and tissues.

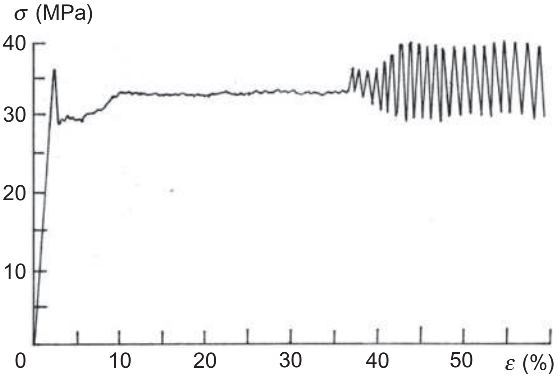

Fig. 1.2 Tension vs. deformation at drawing PET films with constant rate at $T=20°\text{C}$ [16].

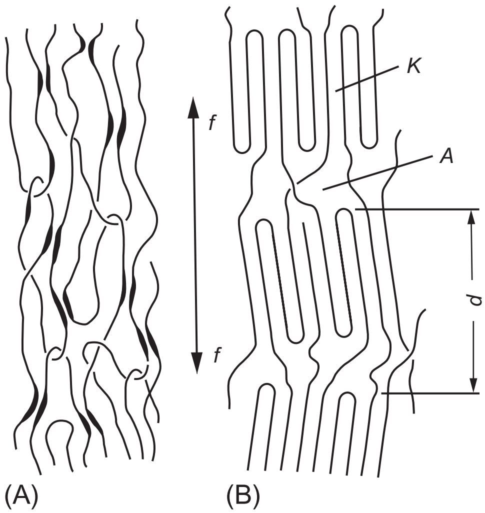

Fig. 1.3 Schemes of fibril structures of glassy (A) and crystallizing (B) polymers. *K* is crystallite, *A* is macromolecules of amorphous phase, *d* is the fibril period, *f-f* is the axis of tension.

Fibrillar structure is inherent to synthetic polymers in the oriented state. SEM images and the data of small-angle X-ray spectroscopy provide for presenting the arrangement of macromolecules in fibrils as shown in Fig. 1.3 [17].

Cross-section dimensions of fibrils are within 1–10 nm; some of their constituting macromolecules are included into the structure of the adjacent fibrils, thus forming the lateral links. The repeating period *d* of fibrils of the crystallizing polymers (Fig. 1.3B) is formed (by 60%–80%) by crystallites. The “passing through” macromolecules that connect them form the amorphous phase, which becomes ordered when heated and is partially included into the structure of crystallites. Under the influence of external force, the passing through molecules are drawn displaying very high strength: the ultimate tensile stress of the straightened macromolecule with C−C bonds is 20–25 GPa [17]. Naturally, the fibril strength is lower, as it depends on the uniformity of load distribution between the fibril-forming macromolecules, i.e., on their stretch ratio, length of macromolecule pieces between the points of fixation, and strength of the latter.

Nanodimensional diameters of fibrils determine, according to the authors of Ref. [1], the possibility to relate such structures to the category of colloidal particles performing Brownian motion. This specific feature of fibrils defines the structure of polymer materials at the final stage of orientational drawing and physico-chemical mechanisms for synthetic fibers modification at the intermediate stages of orientational processing.

Crazes are zones of inelastic deformations localization in polymers in the form of microcracks which walls are connected by the orderly arranged fibrils. The craze structure is schematically shown in Fig. 1.4. It can be seen that the orientational reorganization of polymer material which takes place in the process of drawing occurs through transformation of its initial structure into the highly ordered fibrillar structure.

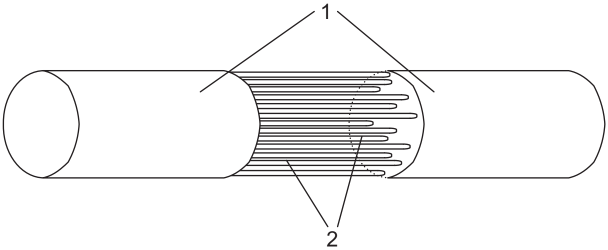

Fig. 1.4 Scheme of the craze structure: 1—parts of the specimen with initial structure and 2—fibrils. The specimen axis of tension is horizontal.

This is a classic case of self-organization of the polymer material whose structure has lost its stability under mechanical load.

Crazing is a totality of physical processes triggered in the polymer material by the external load, which results in the initiation of crazes. The event known as Taylor flow is considered to be a physical mechanism for crazes formation. G.I. Taylor, a British specialist in fluid dynamics, has found instability of the boundary between two incompatible liquids which flow in a narrow channel. The less viscous liquid penetrates the more viscous one, forming a regular system of thin "fingers" in the latter [18]. A similar phenomenon takes place at the crazes formation when the external mechanical stress and the oppositely directed surface forces occurring in the polymer structure create critical conditions under which the polymer is dispersed, forming a system of fibrillar aggregates.

For more than 30 years, the equation based on this theory has been used to describe the polymer crazing [19]:

$$\sigma d = 8\Gamma\sqrt{V_{\mathrm{f}}},$$

where σ is the external stress, d is the diameter of fibrils, Γ is a specific surface energy of polymer, V_{f} is the fibrils volume content in the craze. E.J. Kramer, the author of the above equation, assumed that formation of the crazes is preceded by softening and transition to high-elasticity state of the material at the top of the craze. The action of mechanical stress results in the increase of free volume at local areas of the softened thin (order of nanometers) layer on the microcrack wall and formation of finely dispersed regular phase of fibrils. Kramer's hypothesis, which was ahead of its time, has been confirmed many times, and currently crazing is considered to be a mechanically activated process of local heating and plastic deformation of supramolecular structure which is inherent only to solid polymers [1].

The crazes are initiated on the surface of specimens in the places of mechanical damage and structural microinhomogeneities. The process of their initiation is subject to the thermodynamic criterion which was formulated by the English physicist A.A. Griffith: the destruction is transformed into the surface energy of the newly formed surfaces [20]. It means that crazing is a common property of all polymers irrespective of the degree of their orderliness, and energy characteristics of the surface phenomena accompanying the crazing process are determined, to a great extent, by the properties of the environment.

Collapse of crazes structure is the phenomenon of practically complete transition of the polymer into the fibrillar state at the final stage of crazing. At the collapse, the polymer material reaches its ultimate draw ratio, the specimen cross-section reduces considerably, and its porosity and specific surface area decrease.

1.2 Classical concepts of polymers deformation

Large forced elastic deformations which cause the total transition of a specimen into the oriented state are a unique property of polymers. This phenomenon which forms the basis for the orientational drawing as a basic technology for processing the fibers made from synthetic polymers have been analyzed in detail in various monographs. The attention paid to it in this section is necessitated by the need to complement classical concepts with new data on intermediate stages of drawing which precede the achievement of maximally oriented state by the polymer materials. This particularly applies to the emergence of shear bands of finely dispersed fibrillar structure, crazes initiation, and their collapse in the shear flow process, which are accompanied by the changes in the polymer internal and free energy. These patterns which are called "structural self-organization processes" in Ref. [1] logically conform to the fundamental concepts on the deformation of polymers which are summarized later.

Large deformations developing in polymers under a mechanical load occur due to the change of macromolecular conformations. Energy of the macromolecule thermal motion is insufficient for breaking its bonds with the adjacent conformation-fixing macromolecules. The bonds are damaged when the heat energy is accompanied by the activity of the external force which deforms the specimen. This essential condition for the change of conformations is sufficient owing to availability in the polymer structure of microcavities in which the macromolecule flexibility can be implemented.

General stress-strain diagrams for glassy and crystallizing polymers are given in Fig. 1.5. Their traditional interpretation is as follows [21]. In the proportionality area *I*, the specimens are elastically deformed (up to several tens of percentage) like isotropic bodies. In point A the stress reaches the yield point (forced high elasticity) σ_y, and a neck is initiated in the weakest spot of the specimen. As the tension continues to increase, the nondeformed part of the specimen "migrates" into it (area II). Point B corresponds to the moment when the complete working section of the specimen has

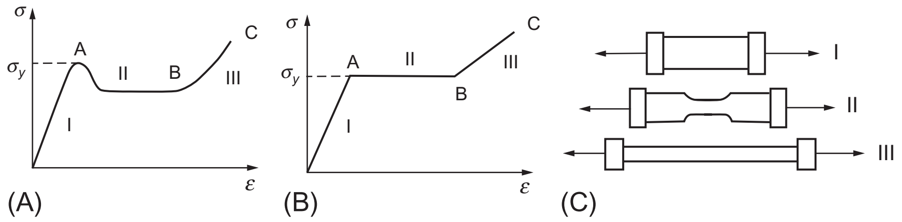

Fig. 1.5 Tension vs. relative deformation of amorphous-crystalline (A) and completely crystalline (B) polymers, as well as the specimen appearance (C) at different stages of tension.

migrated into the neck. In area III, the specimen cross-section reduces even more, but now it is evenly distributed across the full length (as in area I) owing to the increase of both elastic and high-elastic deformations. Their corresponding tensions are distributed unequally across the specimen cross-section, therefore microdiscontinuities appear in them. By the end of area III, they propagate to the full cross-section of the specimen, resulting in its division into two parts and stress decay to zero.

σ_y increases as the temperature decreases. Glassy polymers at temperature $T < T_{br}$ are destructed at small (several %) deformations (Fig. 1.6, curve 1). The σ_y value decreases as the temperature increases and at temperature $T_{br} < T < T_g$ the polymer specimen is deformed as shown in Figs. 1.5A and 1.6, curve 2. At $T > T_g$ the specimen does not display elastic deformation (curve 3), and the yield point σ_y decreases to zero at T_g.

The temperature dependences of the polymer physical states and their corresponding characteristics of deformation are determined by the chemical structure of macromolecules, their mean molecular weight, and their molecular-weight distribution. As an example, we take the temperature ranges of existence of physical states of glassy polymers of different molecular weight (Fig. 1.7). The smaller the molecular weight is, the closer the polymer (by its deformation-strength characteristics) is to low-molecular substances which do not display the forced high elasticity and are subject to brittle destruction. When the molecular weight decreases, point B corresponding to the specimen breaking in Fig. 1.5A moves toward smaller deformations until it reaches point A.

PP and certain crystallizing polymers display large (about 100%) reversible deformations at very low temperatures (near −200°C) when flexibility of the macromolecules is completely suppressed. The deformations are developed at supramolecular level and are not accompanied by the destruction of crystallites structure. In the 1970s, G.M. Bartenev argued that the nature of such deformations is not quite clear [21]. In the following sections it is shown that uneven distribution of stresses at local areas of the polymer structure may be the cause of such abnormal deformations which is confirmed by the changes in internal and free energy of the material being deformed.

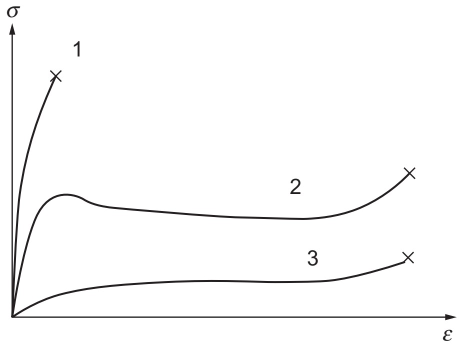

Fig. 1.6 Stress-strain diagrams for glassy polymer at temperatures: 1—$T < T_{br}$, 2—$T_{br} < T < T_g$, and 3—$T > T_g$ [22].

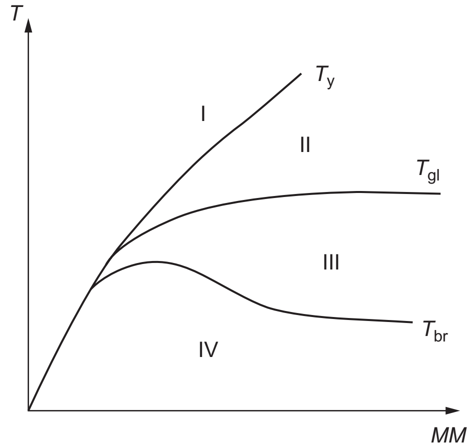

Fig. 1.7 Schematic dependences of the yield temperature, glass-transition temperature and brittleness temperature on the molecular weight of glassy polymer. Areas of physical states: I—viscous-flow, II—high-elastic, III and IV—glassy (IV—brittle fracture) [22].

1.3 Mechanism of crazing in liquids

Inelastic deformation of polymers develops incoherently by localizing subject to the loading conditions in the shear bands or crazes. Both have the clear-cut phase separation boundaries and contain (in their microcavities) the oriented fibrillar structures which determine their morphological similarity [23]. If a polymer specimen is subjected to deformation in low-molecular liquid, it is diffused into the microcavities. This radically changes the physico-chemical mechanisms of deformations development.

Fig. 1.8 shows the scheme of structural transformations of polymer at crazing in liquids. The specimen drawing to the yield point σ_y (stage I) enables the crazes initiation. They are oriented along the normal line to the axis of tension and are of practically same width (fractions of mcm). At stage II, which precedes the moment when the stress-strain curve reaches a plateau, new crazes are not being formed, and the length of the ones already initiated increases quickly. At stage III, the crazes start to spread and the initial polymer structure is transformed into the highly ordered fibrillar state. This process continues until the collapse of the crazes structure and formation of the maximally oriented state of the specimen material.

The liquid is quickly adsorbed on the newly formed walls of the crazes, fills their cavities, and physically and chemically interacts with the polymer material at the top of the craze. The result of this interaction, to a great extent, determines the parameters of the transformed structure and the amount of liquid which penetrated into the microcavities of the deformed specimen. These indicators depend significantly on whether the liquid is the polymer plasticizer or the surface-active environment.

Plasticizers are nonvolatile substances which are thermodynamically compatible with the polymer; when added to the polymer material they provide it with elasticity and/or plasticity. As shown in Ref. [24], drawing in the plasticizing liquid allows an

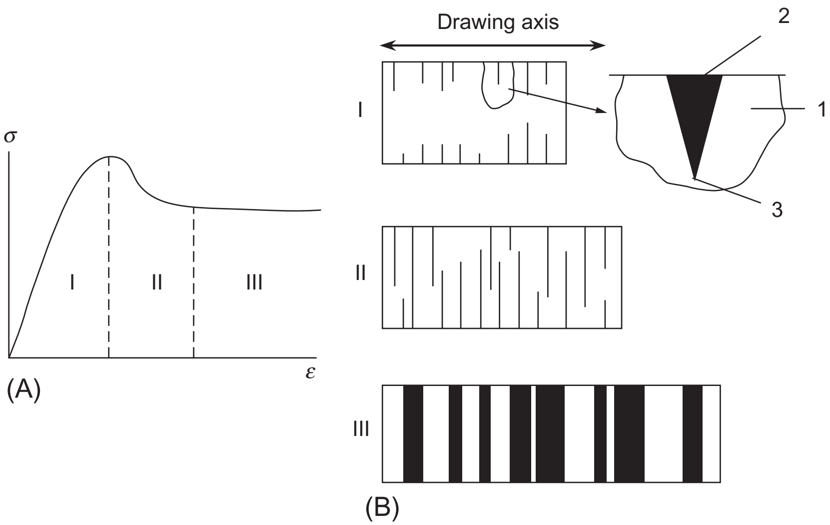

Fig. 1.8 Stress-strain curve (A) of the glassy polymer in liquid and schemes (B) of the crazes development at different stages of the specimen deformation. 1—polymer, 2—liquid, and 3—top of the craze.
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increased swelling of the polymer up to 100% and more. The following is devoted to deformation of polymers in plasticizers.

The surface-active substances (SAS) are capable to be adsorbed very rapidly on the surface of the contacting medium, thus reducing its surface tension and free energy. Crazing in SAS is classical and the most studied type of crazing when the processes of loss in structural stability and self-organization in the polymer are manifested differentially and are convenient for research [25]. Let us study these processes at the stages of the crazes initiation, growth, and spreading.

Crazes initiation takes place most intensively at drawing the specimens in surface-active liquids. Small structural inhomogeneities and mechanical damages of the specimen surface (which do not become initiators of microcracks occurrence at specimen deformation in the air or in the plasticizer) "come into action" when in contact with SAS.

Decrease in the surface energy at the polymer-SAS boundary facilitates the occurrence of microdiscontinuities which turn into crazes (Fig. 1.9A). Density of the initiated crazes (amount per unit of length) significantly depends on the external load value (Fig. 1.9B).

At very small deformations (1%–3%), the crazes initiation has not been registered. Decrease in the specimen drawing rate provides for the decrease in the crazes density. The case when only one craze was initiated in the specimen at an extremely low rate of loading is described in Ref. [26]. The orientational transformations of polymer structure in it have propagated to the full length of the specimen.

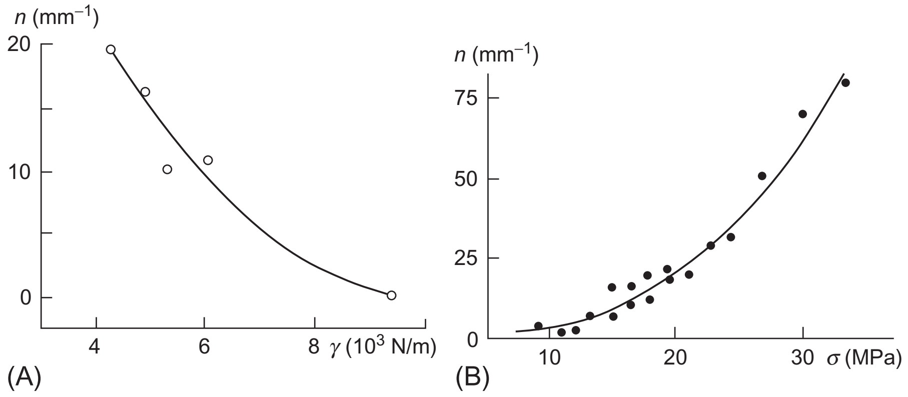

Fig. 1.9 Dependences of the density of crazes initiated at PET drawing in surface-active liquids on the value of: (A) surface tension at polymer-SAS boundary ($\sigma = 23$ MPa) and (B) tensile stress (SAS—*n*-propanol).
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The authors of Ref. [27] determined the *crazes increase in length* by optical microscope having periodically registered the length of crazes initiated in the specimen during the observation. Analysis of these data shows that: (1) each craze grows with constant rate; and (2) the earlier the craze was initiated, the higher its growth rate was. It is conceivable that the driving force behind the craze growth is local tension in front of its top. It is proportional, but not equal to the external stress.

The probability of the liquid penetration into the top of the craze depends on the ratio between rates of its surface diffusion and the craze increase in length. The diffusion rate is determined, to a great extent, by the liquid viscosity. At a high rate of specimen deformation, penetration of viscous liquid into the top may "lag behind" the craze growth. In this case, the crazing process will develop by the mechanism when no liquid is available. The higher the viscosity of surface-active liquid is, the slower the growth of crazes is (Fig. 1.10).

Crazes spreading starts after the neck disappears on the specimen being drawn. An opinion is expressed in Ref. [1] that kinetic patterns of the crazes growth and spreading have much in common. Each craze is spreading with a constant rate at a value individual for it. The crazes growth and spreading are typical activation processes of plastic deformation of polymers. The draw ratio of fibrils formed inside the craze is proportional to the rate of its spreading (Fig. 1.11).

In conclusion, it should be noted that crazing represents one of the stages of inelastic deformation of solid polymers which can develop in various forms depending on the degree of orderliness of polymer material and physico-chemical activity of the environment. As noted before, the natural cause for crazes formation is the polymer transition near the top of the craze into the high-elasticity state. The applied mechanical stress results in an increase of the free volume in high-elastic layer and its transformation into the finely dispersed ordered fibrillar structure [19]. The surface

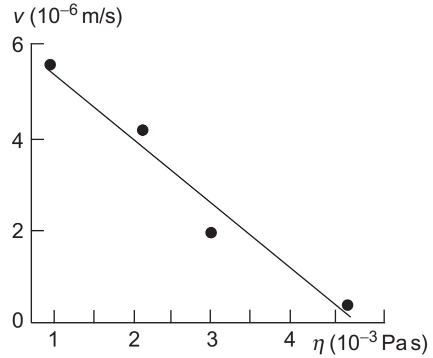

Fig. 1.10 Mean growth rate of crazes in PET deformed in aliphatic alcohol vs. their viscosity. Deformation stress is 17.9 MPa.
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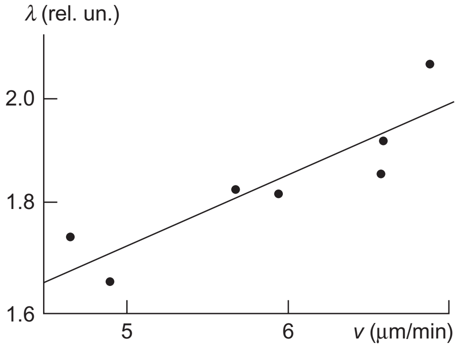

Fig. 1.11 Draw ratio of fibrils inside the craze vs. the rate of its spreading. PET was stretched in ethanol (stress of 12.6 MPa) [28].

activity of the environment optimizes conditions for this process, thus making it less energy consuming.

1.4 Collapse of crazes structure

The spreading of crazes is accompanied by a transition of the initial polymer structure into the dispersed fibrillar state. An array of fibrils, as nanodimensional aggregates of extended macromolecules, has a huge surface area. Its further increase is not advantageous thermodynamically. It is appropriate to consider the final stage of the process of deformation transformation of the polymer structure by the example of crazing in liquids. The process has the following general patterns.

Polymer drawing in liquid is accompanied by its filling the cavities in the crazes fibrillar structure. Fig. 1.12 shows the dependence of the mass of surface-active liquid

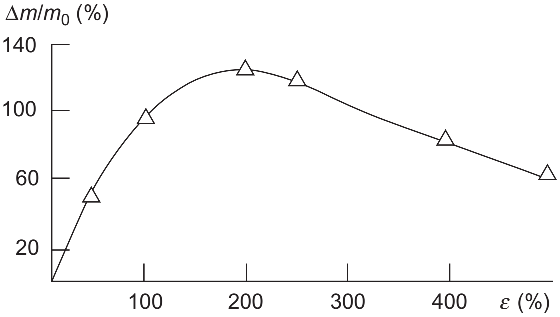

Fig. 1.12 Weight gain of PET specimen vs. its draw ratio in *n*-propanol [29]: Δm—weight gain, m_0—initial weight of the specimen.

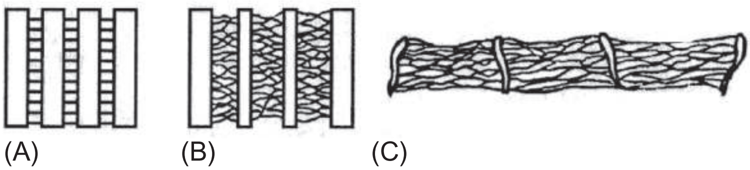

Fig. 1.13 Transformation of the polymer structure at drawing: (A) initiation, (B) growth of crazes, and (C) collapse of the crazes structure.
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(*n*-propanol) absorbed by the PET specimen vs. its draw ratio. The mass of the entrapped liquid corresponds to the volume of cavities in the specimen. The ascending part of the diagram corresponds to the area of deformations at which the crazes are initiated and their volume in the specimen increases. Then the weight gain of the specimens decreases due to development of the processes of shear yield, drawing and convergence of fibrils, and consolidation of the fibrillar structure; as a result, the liquid is squeezed out of cavities.

These patterns are explained by the scheme presented in Fig. 1.13. At the stage of the crazes initiation (Fig. 1.13A), the area of the interphase boundary surfaces is intensively growing in the specimen. An array of the fibrils being initiated in the crazes is thermodynamically unstable. The surface-active liquid in which the specimen is drawn stabilizes the array by reducing surface energy of fibrils and creating kinetic challenges for their movement. At the stage of crazes spreading (Fig. 1.13B), the length and surface area of fibrils, as well as their flexibility and mobility, are increasing. Thermal motion provides for contacting and adhesion interaction between the fibrils. Thermodynamically advantageous increase in intermolecular interaction in the specimen occurs. When the draw ratio is close to the maximum value, further convergence of fibrils becomes impossible, and the specimen cross-section area tends to a minimum (Fig. 1.13C). The specimen acquires the structure of densely packed fibrillar aggregates oriented along the axis of tension. It means that collapse of the crazes structure occurred in the deformation force field.

Polymer drawing in plasticizing liquids has its own specific features. The plasticizer, when entering the top of the craze, promotes formation of a high-elastic layer in which fibrils are initiated. Therefore, the orientational drawing in plasticizers is used to manufacture the maximally oriented films and fibers [30]. The problem was solved by the maximum drawing of PP tapes, which results in the collapse of crazes.

On polymer drawing in plasticizing liquids at the stage of shear flow which is accompanied by the release of heat, the plasticizer is combined with the polymer and decreases its melting temperature. Fig. 1.14 shows the impact of plasticizers of different nature introduced into the crystallizing PP on its melting temperature T_m. It corresponds to the minimum on the temperature curve of the enthalpy change ΔH of the differential thermal analysis (DTA) of the plasticized specimens.

Classical deformation curves of the initial crystallizing polymer and the plasticized materials on its base are presented in Fig. 1.15. Their analysis shows that plasticization immensely stimulates the shear flow of the polymer material [31].

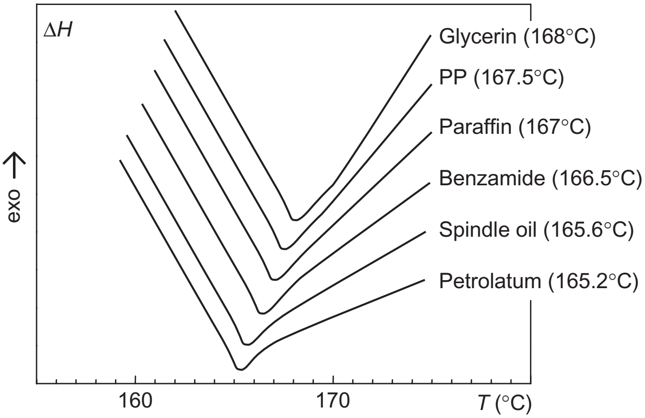

Fig. 1.14 Fragments of DTA spectrums of PP specimens and compositions on its base containing 5% by mass of the plasticizing liquids.

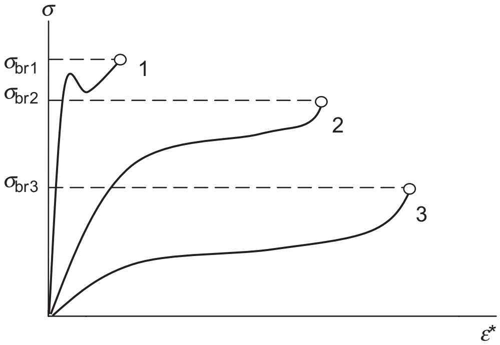

Fig. 1.15 Characteristic stress-strain dependences of amorphous-crystalline thermoplasts: 1—initial, 2—moderately plasticized, and 3—excessively plasticized polymers.

The draw ratio ε^* of PP tapes in the plasticizing Vaseline oil increases as the temperature increases (Fig. 1.16). It is obvious that at $T = 140°C$ the amount of plasticizer that has diffused into the tape is less than at 170°C. Therefore, according to Fig. 1.15, if we succeeded in drawing the tapes to multiplicity factor $\varepsilon^* > 6–8$ at 170°C, they are less strong than the ones drawn at 140°C to the limit value $\varepsilon^* < 6$.

Optical microscope images of PP tapes subjected to drawing are presented in Ref. [32]. Structural inhomogeneities and scratches which developed at the tape drawing from the extrusion head are visible on the surface of tapes in initial state. As noted before, they are the craze initiators. Inhomogeneity of supramolecular structures is registered at cross-sections of the initial tapes: spherulites with a mean diameter of about 10 mcm are localized in the surface layer; the diameter of spherulites is about 300 mcm and larger inside the tape. It is obvious that the surface and middle layers are deformed differently at drawing, resulting in uneven distribution of tensions across the tape cross-section and consequently in initiation of shear bands and crazes. Structures of the tapes drawn to the maximum in air and in plasticizer (glycerin) are significantly different. The tape drawn in air consists of fibrillar bundles on which surface a lot of discontinuities are formed. Similar microdiscontinuities do not appear when the tapes are drawn in glycerin; their surface is smooth, with few defects.

PP drawing in the plasticizing liquids allows to reach a high draw ratio $\varepsilon^* > 15$. The dependence of breaking point σ_{br} vs. the tapes draw ratio passes through a maximum (Fig. 1.17). At the initial stage of shear flow, the increase in draw ratio provides for intensive formation of fibrillar structure and gain in the tapes strength. Further drawing of fibrils is accompanied by microdiscontinuities and strength reduction. The competitive influence of these processes on the tapes strength determines the extreme dependence $\sigma_{br}(\varepsilon^*)$.

The relationship between σ_{br} and ε^* parameters can be divided into two components: a stochastic one which reflects an objectively existing functional dependence

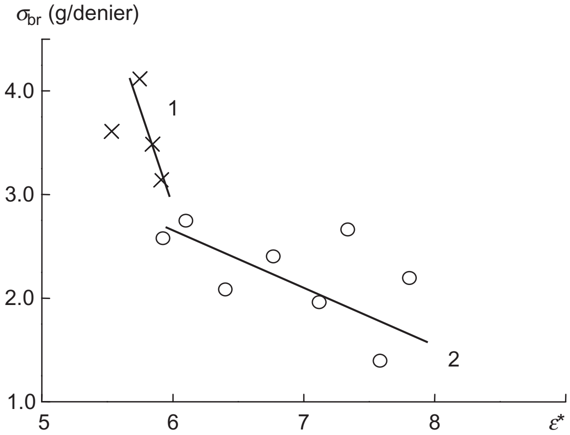

Fig. 1.16 PP tapes breaking point vs. draw ratio in Vaseline oil at temperatures: 1—140°C and 2—170°C [32].

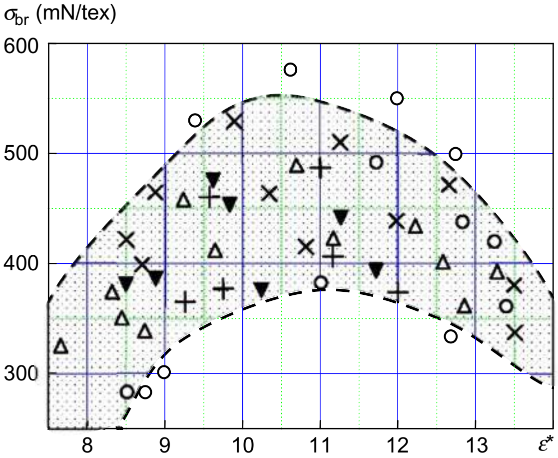

Fig. 1.17 Breaking point vs. PP tapes draw ratio in the plasticizing liquids: ×—Vaseline oil, ○—glycerin, △—benzamide, +—spindle oil, ▼—paraffin [32].

between them; and an accidental one which is generated by the strong impact of statistical factors upon values σ_{br} being registered. Primarily, these are defects of the surface and bulk structure of the tape, nonuniform diffusion of the plasticizer in the changing structure of the tape, impact of the scaling factor at the change of cross-section of the tape being drawn, etc. Therefore, the average relationship between σ_{br} and ε^* is presented in Fig. 1.17 in the form of a shaded area corresponding to the regression equations $\sigma_{br}(\varepsilon^*)$ for different plasticizers.

The result of this research is consistent with the results of X-ray diffraction analysis of the tapes performed with the X-ray diffractometer in monochromatic Cu Kα radiation. There is a twofold increase in the degree of PP crystallinity in the process of tapes drawing. The intensity of the main crystalline peak ($2\theta = 13.85°$) and integral intensity of lines of PP crystalline phases go through their maximum, depending on the draw ratio. When drawn up to $\varepsilon^* = 5.1$, the intensity of the main crystalline peak is maximum, and the amorphous halo disappears from X-ray images. This is evidence of reorganization of the crystalline phase and transformation of the passing-through macromolecules amorphous phase into the oriented one. The draw ratio corresponding to the rapid increase in the amount of microdiscontinuities in the tape structure leads to a noticeable decrease in integral intensity of crystal peaks and growth of the amorphous halo area [32].

Thus, polymer drawing in the plasticizing liquids determines the increase in plasticity of the material in the tops of crazes and intensifies the crazes formation, while the diffusion of the plasticizer in the cavity of the structure being restructured promotes the shear flow development. Molecular plasticization of the polymer results in the reduction of strength of the oriented specimens. Extraction of the plasticizing liquids from them allows to raise the breaking point by 20%–30%. Due to this, the work resulted in achievement of PP tapes specific strength of $P_s = 7$ g/denier (denier being a unit of measure for the linear density of a thread or tape equal to the mass in grams per 9 km of the tape) that corresponds to the breaking point $\sigma_{br} \approx 600$ MPa which is almost 20 times higher than σ_{br} of the initial PP.

In conclusion, it should be noted that the polymer and the liquid (at polymer drawing in liquid) interact continuously, forming a common physico-chemical system. The collapse of crazes is a thermodynamically predetermined result of interaction consisting of a transition from the loose structure of crazes to the compact structure of densely packed nanodimensional fibrils.

1.5 Applied aspects of crazing

A paradoxical idea was expressed in Ref. [1], the implementation of which may radically change the methodology for recycling the worn-out products made of polymer materials. Its essence is as follows. Crazing is the loss in stability of a material's initial structure. Macromolecules have very high chemical resistance; thereby the natural destruction of synthetic polymers lasts for many decades. Thus, destruction of macromolecular structure is of primary importance when recycling polymers. Technological methods for crazing implementation which would allow destruction of the structure of polymeric waste in continuous production process are to be found. Recycling of worn-out tires and rubber products is considered to be the most important area of application of such technology [25].

Technological possibilities for the crazing application during processing of the polymer materials are obviously underestimated at the moment. There is huge stock of processing equipment for orientational drawing of polymer films, tapes, and fibers in the chemical industry. This means that technological operations of inelastic deformation of polymer blanks in the continuous mode can be combined with the crazing without large additional expenses. Let us take the following examples.

Forming of polymer porous sorbents and membranes has long been the subject of a special area of chemical technology [33]. Creation of the system of micro- and nanodimensional pores in the solid blank is a very complex technological task related to overriding the surface forces which tend to reduce the area of interphase boundaries. Crazing allows to solve this problem without using the solvents in the continuous technological process which assures formation of nanoporous polymer adsorbents and membranes for separation of liquid and gas mixtures [34].

Crazing is the universal method to introduce all kinds of substances (even the ones which are thermodynamically incompatible with the polymer) into the structure of polymer materials. Filling the free volume of crazes with the modifying liquids takes place with the rate almost equal to the rate of the crazes initiation. This allows a considerable increase in the concentration of the modifier in the polymer matrix and enables the process to be carried out much more quickly than slow diffusion-sorption mechanism of polymer modification. Active molecular groups are not required in the macromolecules to retain the modifier in the surface layer of the polymer product. Fixation of low-molecular substances takes place by the mechanism of adsorption on the newly formed walls of the crazes and by mechanical capturing of the modifier inclusions by the nanoporous structure of the crazes. Slow (years) release of the nonvolatile modifiers fixed in the crazes is an important factor [35].

Crazing allows modification of the polymer matrix by introduction into its free volume of precursors (parent substances, predecessors) which within in situ chemical reactions impart the matrix with new properties. As the result of crazing, the matrix swelling in precursors increases by two orders of magnitude. In this way, polymer-polymer nanocomposites are produced which phase inhomogeneity is formed at the stage of nanoporosity initiation in the polymer matrix subjected to crazing [36].

The cross-section microrelief can be formed on the polymer films and fibers by crazing. Microphotographs of the sheep wool fibers and PET fibers recycled by the mechanism of crazing are presented in Fig. 1.18. They provide the grounds to formulate a problem of making the consumer properties of products of synthetic fibers closer to properties of woolen products.

The possibility to create regular microrelief of the crazes on the polymer film substrates is used in the technology for producing liquid crystal displays. The relief microhollows provide for fixation of the liquid crystal layer on the substrate. These displays are distinguished by their small weight and slim form, and are not damaged under impact loads [37].

The polymer films subjected to crazing acquire the pronounced properties of piezoelectric materials [38]. This phenomenon laid the foundation for development, under the guidance of the German physicist G. Sessler, of the production methods and the design of electric sensors for electronic instruments. Crazing of the films with thin metallic coatings is the basis for methods for forming elements with the defined optical density for optoelectronic instruments [39].

According to A.L. Volynskii, formation of the microrelief in the polymer films subjected to crazing is similar to the loss of stability of the surface layer of the natural objects of hard-coating-on-a-pliable-base structure: fruits (tomatoes, apples), human

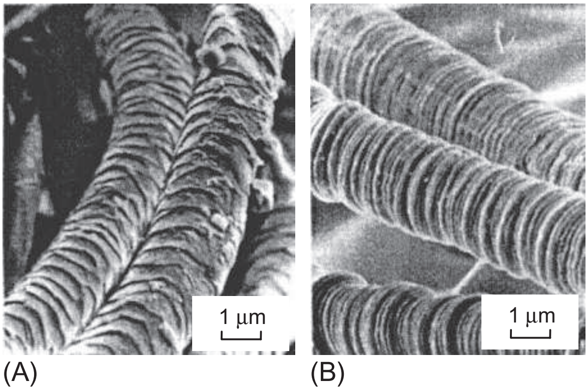

Fig. 1.18 SEM images of: (A) sheep wool fibers and (B) PET fibers subjected to crazing. Reproduced from Volynskii AL, Bakeev NF. Structural self-organization of amorphous polymers. Moscow: Physmatlit; 2005. 232 p. with permission from PHYZMATLIT Publ. House.

and animal bodies, the Earth's crust, etc. Reliefs, similar to the ones observed at deformation of polymer films with thin hard coating, evolve under the influence of tectonic stresses on the hard crust of the Earth (lithosphere) [40].

The following chapters describe application of crazing as a physical-chemical basis for technologies of synthetic fibers modification and discuss the results of industrial implementation of these technologies to produce special purpose PET fibers—bactericidal and bacteriostatic, of reduced combustibility, repellent, for protection of securities, as well as radio absorbing, aromatized, and antistatic ones.

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Modification of synthetic fibers

2

An extensive array of methods to regulate the synthetic fibers' structure and properties which is used at practically all stages of fibers formation has been developed for chemical industry.

The fibers covered by the book are formed by drawing the polymer melt through spinneret openings of the extrusion head. The polymer material being extruded shall have mean value of molecular weight not exceeding 150 kDa (Dalton, or AMU equal to 1/12 of the mass of carbon nuclide ^{12}C) and narrow molecular-weight distribution to ensure technologically feasible melt viscosity ($\eta \approx 50$–$150\,\mathrm{Pa\,s}$). The structure of fibers' crystal phase is regulated by varying the temperature and drawing speed of the melt, conditions of cooling the fibers in viscous-flow state and aerodynamic drag against their movement from the head [1]. By applying special extrusion heads, profiled fibers which cross-sections have a shape of an oval, sprocket or polygon, as well as bi-component fibers of “side by side,” “nucleus shell” type consisting of two polymer materials or different brands of one polymer differing in molecular weight are formed [2,3].

In the course of orientational drawing, the majority of synthetic fibers acquire fibrillar amorphous-crystalline structure with crystallinity of 50%–95%. Their stress-strain characteristics are best determined by the number, orientation, and various lengths of passing through macromolecules [4].

Properties of the fibers' polymer base are adjusted by filling or plasticization methods. Properties of the surface layer, which determines hydrophilic behavior, color yield, biostability, antifrictionality, ability of fibers to discharge static electricity, etc., are directionally changed by inoculation of functional groups to macromolecules [1], as well as by processing the fibers with the so-called textile-auxiliary chemicals (avivage substances, sizing agents, oiling agents, coupling agents, antistatic substances, etc.) [5].

The colored fibers are obtained by extrusion processing of specially prepared granules, filled or “powdered” with solid particles of dye or swelling in their solution. Dyeing of polyester fibers is mostly carried out by diffusion processing under pressure in the dyeing solution. To ensure color stability, it is necessary to implement physico-chemical fixation of the dye molecules at the active centers of polymer material [6].

Modifiers of different nature are traditionally introduced into synthetic fibers by using these basic methods and a range of their varieties. Therefore, solid fine-dispersed particles of targeted additives are “pasted” on the fibers when they are in viscous-flow state at the extrusion head outlet by using circular [7] or flat [8] gas-powder flows. Adhesive components are used to improve reliability of particles fixation on the fiber. They are even introduced into the modifying compounds in which fibers are drawn [9].

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2.1 Overview of synthetic fibers

Fibers and fibrous materials address human needs in clothes and household, technical, agricultural, medical, and other products. Synthetic fibers have become as important as natural fibers which have a millennia-old history of production and utilization. They became one of the main large-tonnage products of polymer chemical industry. In 2014, world production of chemical fibers reached 63 million tons (including 57 million tons of synthetic ones), while the production of natural fibers amounted to 30 million tons (Table 2.1). This trend is strengthening in the current decade.

In the 21st century, polyester, polyacrylonitrile, polyamide, and hydrated cellulose (mainly viscose) have become the main types of synthetic fibers and threads. Respective niches in the production technology and ranges of application have been determined for each of them.

In the last three decades, polyester fibers and threads hold leading positions by production volume and growth rates. Starting from 2000, they are leaders not only among chemical fibers (about 80%), but also among all types of textile raw materials (about 40%) [11,14]. Naturally, the global situation depends on contributions of regional manufacturers, which vary widely [14]. Asian countries account for 88% of the world market of synthetic fibers, of which the share of China is 62%. Monoethylene glycol and terephthalic acid which production is significantly cheaper in the countries in Asia are used as raw materials for polyethylene terephthalate (PET). The Chinese chemical industry plans to increase capacities further for production of polyester fiber, to more than 3 million tons a year. An increase in production of polyester textile threads is due in large part to an increase in their consumption by the outdoor clothing industry. According to the assessment of experts, in 2015 the global production volume of polyester staple fiber will amount to 18 million tons, including 14 million tons produced in China [12].

Polyester fiber, while keeping its leading position among all types of fibers, is the sole one with the growing share of consumption and exerts the greatest influence on development and potential of allied industries. The current analysis of production and predictive estimate of the world consumption of various types of fibers till 2015 shows a steady trend of increased demand for polyester threads and staple fibers [12].

The favorable combination of natural, socioeconomic, transport energy, and intellectual factors favored the intensive development of synthetic fibers industry in Belarus

Table 2.1 World production of textile fibers [10–13]

Types of fibers	Year-wise production (million tons)					
	2000	2010	2011	2012	2013	2014
Chemical, total	31.0	45.2	52.7	56.0	60.3	63.3
Synthetic	28.4	45.2	47.9	51.0	54.4	57.1
including polyester	19.6	33.3	38.9	39.0	40.4	42.1
Natural, total	26.1	28.3	30.3	30.4	28.2	31.1

in the 1970–90s. In 1990, production and processing of synthetic fibers provided for more than 18% of its national income [15]. Despite the production slump due to the demise of the Soviet Union, by the beginning of the 21st century the enterprises producing chemical fibers in Belarus (although their production volume decreased by 2.2–2.5 times compared to 1990) maintained their output at the level of 220,000 tons. Belarus is the undisputed leader among CIS countries: in 2010 its production volume of synthetic fibers exceeded Russia's by 100,000 tons [12]. Therefore, Belarus remains the supplier of synthetic fibers to the Russian market. In 2002, the share of synthetic fibers supplies to Russia (although decreased by 7% when compared with previous year) remained at a high level: 86% (61,300 tons) of the total amount of Russian import [16]. This trend appears to have continued up till now.

The Belarusian industry of synthetic fibers was created and developed to accommodate the needs for fibrous raw materials of the economy of all USSR republics. Consumption of own products in Belarus did not exceed 10%–15%. Currently, the share of chemical fibers being processed in the country amounts to about 20% of the production volume. Starting from 1999 the production of chemical fibers, including polyester ones, has been constantly growing and in 2011 it increased by 18.9% as compared to 2009 with the capacity utilization rate of 84.9%. This is mainly due to an increase in production of [12]:

- polyester industrial threads (by 58.3%), staple fiber (24.4%), spunbond (34.1%) at JSC Mogilevkhimvolokno;
- polyester textile threads (by 8.7%) at JSC SvetlogorskKhimvolokno;
- polyamide industrial and cord threads (by 11.2%), bulked continuous filaments for carpet applications (46.1%), cord fabric (12.8%) at JSC GrodnoKhimvolokno; and
- staple PAN fibers (by 6.2%) at JSC Naftan.

In 2012, JSC GrodnoKhimvolokno doubled their production capacities for polyamide carpet threads. In 2010 the share of these products amounted to 35% of the total industrial output. Serial production of polyamide twisted thermoset threads for manufacturing elite carpets was started in 2011.

The analysis of prospects for development of chemical fibers production should incorporate a number of determinant factors, primarily the condition of processing equipment. Modern equipment and new material- and energy-saving technologies are required to increase the range of fibers and threads and produce new types of products demanded on the market. Technical and economic prospects for development of the chemical fibers industry in Belarus are complicated by physical deterioration and obsolescence of the main technological equipment and process communications. Therefore, reconstruction and modernization of the production of polyester textile threads is underway at JSC SvetlogorskKhimvolokno; when it is finished the enterprise should become one of the leading companies in this field in Europe. New equipment for manufacturing threads (composite, equilibrium and equal-length, textured, pneumoconnected ones with the adjustable strength and number of nodes) was commissioned. An original technology for dyeing polyester threads is implemented. In 2010, a new line for threads formation (capacity up to 38,500 tons a year with the ability to process up to 24 various types of threads) was commissioned. Texturing machines were installed in Svetlogorsk with the participation of Japanese companies Marubeni and TMT Machinery.

Fibers on the base of PET are the main type of polyester fibers. Prospects for priority development and use of PET (lavsan) fibers pertain to the uniqueness of structure and properties of PET as compared to the other types of fibers [17]. Hi-tech PET fibers are characterized by high-mechanical characteristics as compared to the natural fibers and many types of chemical fibers which comparative indicators are presented in Table 2.2.

The possibility for the targeted change of mechanical characteristics of PET fibers is predetermined by the degree of orientational drawing. Intermolecular interaction of fibrils, degree of crystallinity, and density of fibers [18,19] increase along with the growth of the fiber orientation. Mechanical characteristics of the dampened fibers remain practically unchanged [20]. High degree of elastic recovery of fibers determines the form stability and low creasing properties of lavsan fabrics, while stability of PET structure provides for low shrinkage [4]. Textile fibers and threads made of PET can withstand (without noticeable change in properties) temperatures up to 150–160°C, and highly ordered industrial threads—up to 170–180°C [17].

Chemical stability is a valuable property of PET fibers. Small dipole moments of monomer units in macromolecules, high density of packing at the supramolecular and fibrillar levels, low reactivity of ester group of macromolecules make the fibers difficult to be accessed by many chemical agents [21]. The same features of PET structure determine the fibers' resistance to atmospheric impact, their biostability, and their biological inertness [4,17,21].

PET fibers have the following shortcomings: poor color yield, electrifying ability, low hygroscopicity, and pilling (formation of small tangles of fibers or “balls” on the surface of fabric). In order to overcome these, methods of chemical and physical modification of PET are applied [4,21]. Owing to an introduction into monomer (at the stage of synthesis) of a comonomer containing ionogenic sulfonate groups, PET acquires an ability to dye molecules due to appearance of new polar groups in the macromolecule [22]. For the purpose of increasing the color yield, the alkaline hydrolysis reaction is used which takes place on the fiber surface (“O-finishing”) [23] or dyeing intensifiers are applied which role is to decrease the glass-transition temperature, “loosen” the supramolecular structure to a certain extent, and increase the rate of the dye diffusion into the polymer [24]. During “O-finishing,” the fibers hygroscopicity increases (along with the increase of the color yield), while electrifying ability and peeling decrease [25].

Textile materials made of mixtures of polyester and other fibers which preserve the advantages of polyester fibers are being widely used. Most often, lavsan fiber mixtures are combined with cotton, flax, and wool at a ratio ranging from 35/65% to 50/50%. In the fabrics manufactured from such mixtures, PET fibers act as the component which increases the shape stability and wear resistance, and low hygroscopicity of fabrics is offset by cellulose or woolen component [17].

The range of PET-based products is very wide [10,14]:

- staple and textile fibers (monofilament threads, complex, profiled, textured, multifilament threads, microthreads and microfibers, bicomponent threads);

Table 2.2 Comparative properties of natural and synthetic fibers [4,17,18]

Type of fibers and threads	Property indicators						
	Density (g/cm^3)	Strength (sN/tex)	Elongation at rupture (%)	Elastic recovery (%) (at deformation of 4%–5%)	Hygroscopicity (%) (at $\varphi = 65\%$)	Degree of swelling in water (% by mass)	Strength retention after swelling (%)
Cotton	1.52–1.56	22–36	8–13	~45	7–9	40–50	110–115
Woolen	1.3–1.32	10–15	30–60	78–95	13–15	45–65	70–80
Viscose	1.5–1.56	16–25	19–26	35–45	11–14	100–120	50–55
Polyamide (capron)	1.13–1.14	30–45	40–50	100	4–5	10–13	85–90
Polyester (lavsan)	1.38–1.39	36–48	30–55	98–100	0.3–0.4	3–5	~100
Polyacrylonitrile (Nitron)	1.17–1.18	20–30	30–45	65–70	0.8–1.5	3–6	92–95

- high-strength industrial threads with linear density 6–14 to 1000–10,000 tex, fibrillated and tape yarns with linear density 100–5000 tex, monofilament threads (diameter 0.1–2.0 mm and larger) to manufacture loaded textiles (cables, ropes, belts, tapes), filter fabrics and packing cloth, overalls, auto tires reinforcement, conveyor belts, high-pressure hoses;
- data storage media: films for cinematic, photographic and X-ray purposes, hard drives (Winchester disk drives) and floppy disks used in computer hardware, magnetic tapes for audio, video, and other recording equipment which were produced in large quantities until recently;
- containers for liquid products;
- critical types of polymer composite products for mechanical, electrical, and radio engineering; and
- sheet material used in agriculture and construction.

2.2 Specifics of polyester fibers crazing

The methods for fibers modification applied in the textile production assume that the polymer material and the modifier are thermodynamically or technologically compatible [20]. The use of the crazing technology presents grand possibilities: firstly, to overcome the components incompatibility and, secondly, to introduce the modifier only into the surface layer of the fiber. Development of such technologies is complicated by insufficient data on the patterns of synthetic fibers crazing in textile-auxiliary liquids.

At the stage preceding the development of industrial technologies, experimental studies on the patterns of the crazing process in PET fibers were performed in MPRI NAS Belarus.

The PET fibers crazing process in cationic antimicrobial liquids Katamin AB and Althosan MB (active substance of which is alkyl dimethyl benzyl ammonium chloride) was studied. Fibers were stretched in contact with liquid under the visual control of an optical microscope. The stretched fiber was fixed on electrically conductive adhesive tape; a layer of gold was then applied on it by ion-assisted deposition method. The specimen prepared as above was studied by means of a scanning electron microscope (SEM) NEGA//TESCAN equipped with Digital Microscopy Imaging software.

Microphotographs of such fibers are presented in Fig. 2.1A and B. Area I (where tensions lower than PET yield point are developing) is the place of crazes initiation. Area II corresponds to the beginning of PET plastic flow, initiation of a neck on the fiber and growth of the crazes. Intensive formation of the neck in area III provides for crazes spreading. In area IV the fiber structure consists of fibrils. Fig. 2.1B shows the enlarged photo of one of the crazes. It can be seen that walls 2 of crack 1 are connected with fibrils 3. A structural diagram of the formation is presented in Fig. 2.1C. A further drawing of the fiber is accompanied with gradual transition of the source material of the fiber into the fibrillar structure of fibrils [26].

It is obvious that saturation of crazes with liquid occurs most intensively in areas II and III which correspond to the neck formation. In area IV the entrapped liquid is redistributed within the fiber structure. The content (determined by the weight method) of modifying liquids of different densities in the fibers subjected to crazing amounts to 0.9%–3.3% by mass.

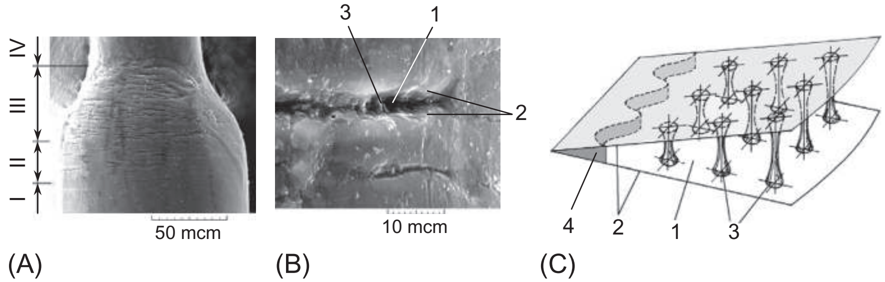

Fig. 2.1 SEM images (A, B) and diagram (C) of crazes formation in PET fibers. Roman numerals indicate the areas of the fiber tensioned state where the following occurs: I—crazes initiation; II—growth; III—crazes spreading; and IV—formation of the fiber fibrillar structure. 1—crack; 2—crack walls; 3—fibrils; and 4—layer of high-elastic material at the tip of the crack.

Availability of bactericides in the specimens of fibers subjected to drawing in Althosan and Katamin is confirmed by infrared spectroscopy and X-ray diffraction method [27]. Essential changes in intensity of absorption bands of IR spectra of the fibers occur in the range of frequencies 2800–3600 cm^{-1}. These areas correspond to valence vibrations of nitrogen-containing (3300–3500 cm^{-1}) and CH_2 groups (2850 and 2908 cm^{-1}) in bactericides (Fig. 2.2).

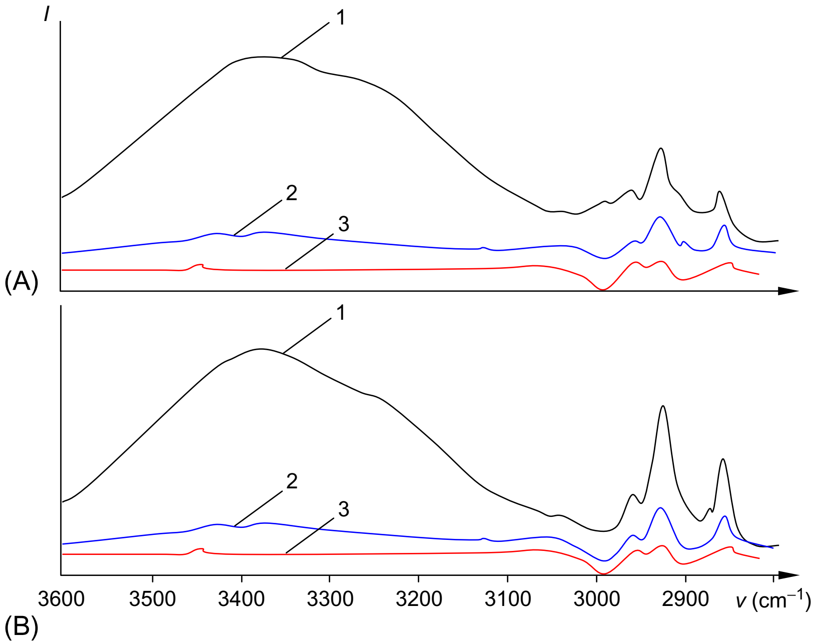

Fig. 2.2 Fragments of IR spectra of the absorption of antimicrobial modifiers (A, Althosan; B, Katamin) and PET fibers into which they have been introduced by the mechanism of crazing (draw ratio $\varepsilon^* = 3$). 1—modifier; 2 and 3—fibers subjected to drawing in the modifier and source fibers.

The analysis of X-ray spectra of the fibers under study has shown that the position and intensity of PET crystal peaks do not change at modification. At the same time, amorphous halo of PET identified with the help of X-ray software are not identical in position and max values for Althosan and Katamin. This represents the fact that diffusion of liquids entrapped by the crazes occurs mainly in noncrystalline phase of fibers.

When selecting the composition of modifying liquids and technological modes for fiber drawing in them, it became necessary to use a device which would allow the monitoring of the crazes' initiation, the place and time of their initiation, and the extent of opening. We have developed and manufactured the device to monitor (by the method of optical microscopy) the process of crazes formation and growth in a single monofiber with possibility to adjust its draw ratio and to apply liquids of different surface activity on the stretched fiber [28]. It is similar to the device used to monitor the growth of microcracks in the films placed into liquid [29]. Distinctive features of the new device are: (1) quantitative control of the processes of crazes formation and growth; (2) improved accuracy of the specimen draw ratio adjustment; and (3) the possibility to apply the liquid being studied onto the specified area of the stretched specimen.

The design of the device implies its installation on the object table of optical microscope. The device presented in Fig. 2.3 consists of a cylindrical foundation (1) with a milled longitudinal slot (2). Two racks (3) with aligned openings are rigidly attached to its bottom. A screw (4) (capable of rotation) is installed into them. The screw has

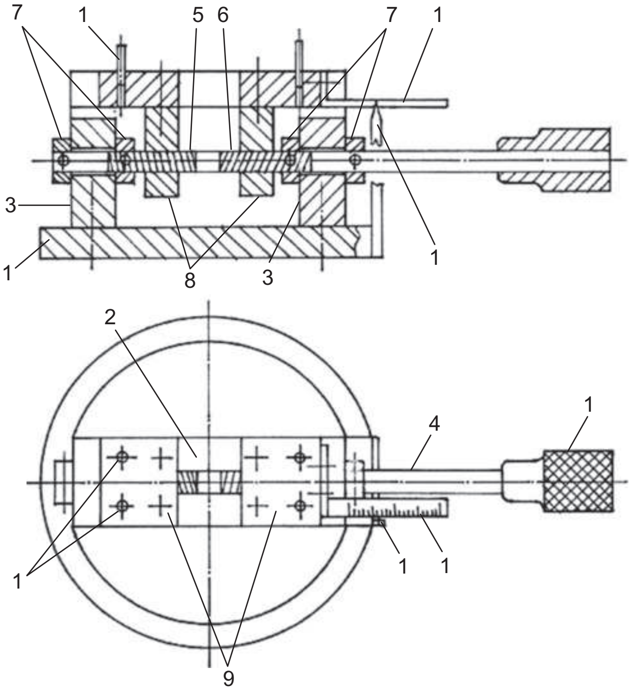

Fig. 2.3 Design of the device for studying the microcrazing kinetics.

areas (5 and 6) with left-hand and right-hand threads. Lock washers (7) are fixed on the screw on both sides of the racks (3) to prevent its movement along the axis. Sliders (8) are movably interlinked with the threaded parts of the screw (the left-hand or right-hand thread is cut respectively in the openings of the sliders). Plates (9) which are conjugate to the walls of the slot (2) along the running fit are fixed to the upper ends of the sliders. A pair of racks (10) for fixing the fiber specimens is installed on each plate. A handle (11) is rigidly fixed on the outer end of the screw (4). A ruler (12) (scale division 0.1 mm) is attached to the edge of a plate (9) located at the handle side. An arrow (13) of which the head touches the ruler (12) is fixed on the same side at the lower end of the foundation.

The device works as follows. The plates (9) are brought together until their edges come into contact by the rotating screw (4). The fiber under study is fixed in racks (10) installed on different plates. The plates are pulled apart by rotating the screw, thus the fiber is stretched. At the same time the specimen deformation changes (neck formation in the fiber, initiation of crazes, etc.) are monitored. The specimen draw ratio is determined by the change in the arrow's (13) position with respect to the ruler (12) (which is registered using a microscope) with an accuracy of 5%. Microdrops of liquid under study are applied on different areas of the stretched fiber with a syringe. Changes of the fiber surface layer (visible under the microscope) are monitored.

Possibilities of the device largely depend on the microscope resolution. The following has been chosen as the result of comparing the crazes quantity and extent of opening in different areas of the fiber stretched with different intensity before and after application of the liquid under study:

- the place where liquid and fiber are to be brought into contact (optimal according to the crazes formation criteria);
- the fiber draw ratio providing for a rather dense grid of crazes; and
- a group of the surface-active liquids which initiate crazes formation with the increased intensity.

The results of such assessment allowed to preliminary determine the ranges of acceptable values for technological parameters of drawing; then these results were defined more accurately using SEM.

2.3 Techniques for synthetic fibers modification by crazing mechanism

The methodology of crazing provided a basis for a highly effective technological approach to creation of nanocomposite synthetic fibers. The crazing enables the thermodynamically favorable process of emergence of regular nanocavities in the fiber and possibility to introduce any modifiers irrespective of their nature into them under the technologically feasible conditions of the fibers deformation (tension, physical and chemical activity of the modifying liquid, temperature, drawing speed, etc.).

The technology for modifying polymer products by the mechanism of crazing was protected by US patents in the 1960–70s (3102233 and 3233019, authored by Adams;

4001367 and 4055702, Gutrie et al.). A patent [30] is the later version in which the term *cracking agent* (chosen by Adams) is substituted with the terms *crazes* and *imbibition drawing*. The patent protects the method for processing the long-length products made of polymer materials in the modifying liquid possessing surface activity.

The first in CIS variant of such technology and the device for its implementation [31,32] was developed by groups of scientists from Chemistry Department of Lomonosov Moscow State University and the Russian Scientific Centre Kurchatov Institute. They were implemented in industrial production of fire-retarding fibers (JSC Poliholding, Russia), as well as thermal and sound insulating materials for construction (JSC Vladpoliteks). The technology is the know-how of these organizations. The task of mastering the crazing technologies to produce competitive (in comparison with the products made in China, Malaysia, Turkey, etc.) domestic textile products is a challenge for Belarus, which has a network of large enterprises for synthetic fibers production (members of the concern Belneftekhim). Characteristics of the main stages for solving the task are given below.

The process of synthetic fibers modification by the mechanism of crazing consists of the following operations:

- feeding the fiber to the stretching unit, forming a spool rack (set of spools with the fiber to be processed);
- passing the fiber through the bath with the oiling agent;
- passing the fiber (at the initial stage of drawing) through the node of modification by the mechanism of crazing—“crazing module”;
- continuing with the fiber drawing in the steam chamber where the fiber is also dried and heat set; and
- cutting (at the staple fiber output), packing of the modified fiber.

Larger specific number of crazes provides for larger amount of the modifier introduced into the fiber structure. The basic amount of the modifying liquid is captured by the fibers at the stage of crazes spreading prior to the beginning of their collapse. A further increase in the draw ratio may cause microdiscontinuities in the fibrillar structure of the fibers. Therefore, the following technological parameters of the modification process are the determining factors: draw ratio, speed of the fiber passing through the crazing module, surface activity of the modifying liquid, the nature and concentration of the modifying substance in the liquid, and its temperature. In each particular case, values of the mentioned parameters are selected empirically depending on the type of the fiber raw material, design of the crazing module, and required characteristics of fibers.

We shall now analyze the pros and cons of the main design and technological options for fibers modification by the mechanism of crazing. Five schemes of bringing the fibers being drawn and the modifying liquid into contact are discussed below, and these are:

(1) spraying method;
(2) rotaprint method;
(3) by means of capillary heads;
(4) watering method; and
(5) submersion into a bath.

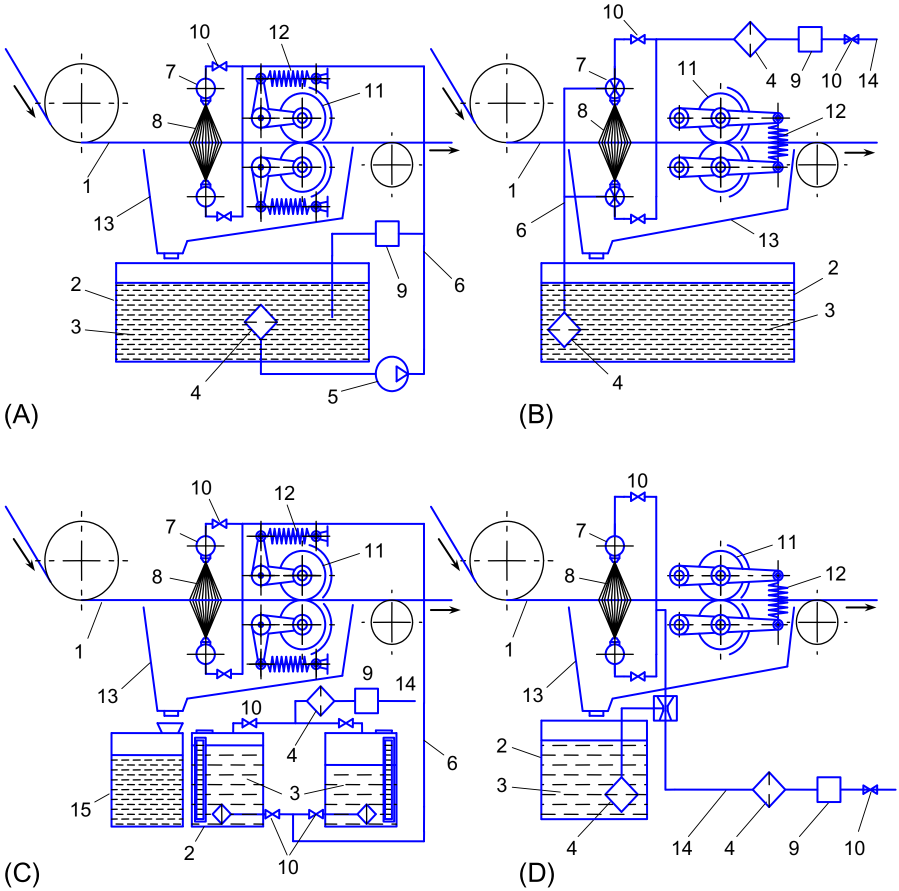

Fig. 2.4 Applying the solution to fibers by spraying with liquid (A) and gas-liquid (B–D) nozzles: 1—bundle; 2—tank; 3—solution; 4—filter; 5—pump; 6—liquid line; 7—nozzle; 8—flare of the sprayed solution; 9—pressure reducing valve; 10—flow regulator; 11—roller; 12—spring; 13—tray; 14—compressed gas line; 15—accumulating unit; and 16—disperser.

2.3.1 Spaying method

Spraying of the modifying solution is exercised using liquid and gas-liquid nozzles (Fig. 2.4). Short description of the methods for applying a solution onto the fibers is given below.

According to Fig. 2.4A, true or colloidal solution of the modifier is pumped from an open tank to the liquid nozzles located above and below the bundle of fibers being drawn. Pressure reducing valve is used to maintain the specified pressure in the spraying system. Fluid flow regulators are installed before the nozzles. A pair of spring-loaded rollers is installed behind the spraying area; the rollers are intended for distribution of the solution across the bundle width to ensure its forced penetration into the gaps between fibers and squeezing out the excess solution. An upper roller can be lifted to insert a bundle. The excess liquid flows down into the tray and returns to the tank.

Fig. 2.4B differs from Fig. 2.4A by the use of gas spraying nozzles. The solution is fed to the nozzle owing to vacuum which is formed at the discharge of the airflow. Pressure and flow regulators and a filter are installed in the compressed gas line.

According to Fig. 2.4C, liquid nozzles spray the solution fed from the tank in which the excessive pressure is created by the compressed gas. One of two feeder tanks is used in sequence (switching-over is exercised using the valves). The excess solution is collected in the tray and flows down into the accumulating tank.

Fig. 2.4D is intended to modify the fibers by means of the gas-emulsion flow generated in the high-speed disperser. The emulsion concentration in the flow can be changed by varying gas pressure and emulsion flow being fed to the disperser.

Disadvantages of the devices in which spraying method is implemented include:

- uneven distribution of the solution across the bundle width;
- increased energy consumption to create high pressure at the solution inflow into the nozzle;
- the need to filter the solution and carrier gas to prevent contamination of the nozzles;
- expediency to maintain a constant level of the solution in tanks with excessive pressure (Fig. 2.4B–D); and
- complicated design of the devices containing two tanks (Fig. 2.4C), a tank with emulsion and disperser (Fig. 2.4D).

2.3.2 Rotaprint method

The term “rotaprint” originated from the printing industry. It means the transfer of printed characters to paper with the form fixed on a rotating roller. The thickness of the ink layer (of the characters applied on the form) is sufficient for repeated printing.

The rotaprint method for applying textile-auxiliary chemicals is traditionally used in processing natural and chemical fibers [2,5].

The rotaprint method of crazing technology implies the fiber drawing with two systems of rotating rollers: “slow” and “fast” ones. The modifying solution is continuously applied on the surface of the last roller of the “slow” system which transfers the solution to the fibers at the start of their drawing. The efficiency of the fibers modification by the rotaprint method depends on the following factors: wetting of the roller contact surface, speed of the roller rotation, temperature, thickness of the solution films on the roller, etc. Fig. 2.5 shows the main schemes of synthetic fibers modification by the mechanism of crazing with the rotaprint method. Please note the following comments.

Fig. 2.5A envisages the use of two rotaprint rollers: the lower one is submerged into a bath with solution, and the upper one covers the bath aperture and is equipped with a sealing which allows a thin layer of the solution to reach the roller surface. The liquid level in the baths is kept constant via overflow baffles. The solution is pumped to the baths from the common tank. The common tank is also used to collect the excess solution which is drained from the tray and pressure reducing valve. A pair of spring-loaded squeeze rollers has the same function as described in the caption to Fig. 2.4A.

According to Fig. 2.5B, the bundle passes around three “slow” rollers which are in contact with each other. The solution is fed by spraying into the gap between the first

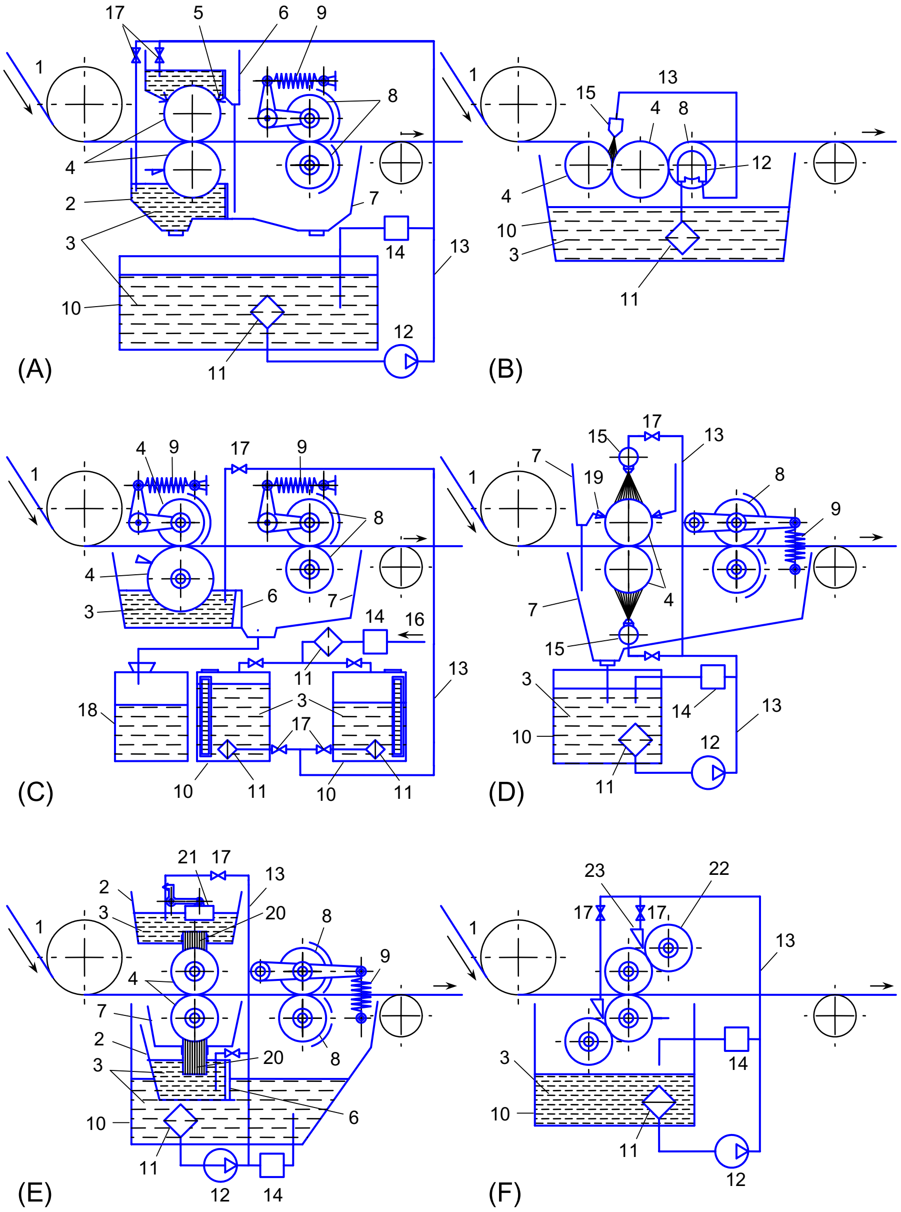

Fig. 2.5 (A–F) Applying the solution onto fibers with rotaprint rollers: 1—bundle; 2—bath; 3—solution; 4—rotaprint roller; 5—sealing; 6—overflow baffle; 7—tray; 8—squeeze roller; 9—spring; 10—tank; 11—filter; 12—pump; 13—liquid line; 14—pressure reducing valve; 15—nozzle; 16—compressed gas line; 17—flow regulator; 18—accumulating unit; 19—blade; 20—capillary-porous element; 21—float-type device; 22—auxiliary roller; and 23—fitting.

and second rollers via the pump installed on the third roller axis. The excess solution flows down into the tank. The first and third rollers can be shifted in horizontal direction to insert a bundle.

According to Fig. 2.5C, only lower rotaprint roller of the pair is submerged into the solution. A pressure roller is installed above the bundle of modified fibers. A constant level of liquid in the bath is maintained by overflow of the excess liquid via a baffle. The solution is fed to the bath from the tanks which are under compressed gas pressure. The additional pair of spring-loaded squeeze rollers ensures uniform distribution of the solution in the bundle.

According to Fig. 2.5D, upper and lower rotaprint rollers are wetted with the solution sprayed through the nozzles. The upper roller is equipped with a blade to create uniform layer of liquid on the roller surface. The solution is pumped to the nozzle from the tank. The excess solution flows down to the tray and then to the tank. The excess liquid is removed from the bundle with a pair of squeeze rollers.

Fig. 2.5E envisages wetting of rotaprint rollers with the solution using capillary-porous elements installed in the service baths. The solution is pumped into the baths. The liquid level in the upper bath is maintained by means of a float-type device, in the lower bath—by overflow via a baffle. The solution is fed to the upper roller under hydrostatic pressure of the solution in the upper bath, while the feeding to the lower roller is exercised under capillary forces. The excess solution flows down into the tank.

Fig. 2.5F envisages two pairs of rollers. The rotaprint and auxiliary rollers of each pair are in contact. A flat jet of the solution is fed through a special fitting into the rollers' contact area. The solution is pumped to the fittings from the tank.

Disadvantages of the rotaprint devices include:

- design complexity of the systems for lifting upper rollers to insert a bundle (Fig. 2.5A, E, and F);
- the need to install contact sealings (a), pressure regulating systems between rotaprint and auxiliary rollers (Fig. 2.5B and F), blade node (Fig. 2.5D); and
- complexity of selecting materials for capillary-porous elements and design complexity of the devices which ensure optimal pressure in the place of the elements' contact with rotaprint rollers.

Installation for threads dyeing is an example of how basic schemes of the fibers' rotaprint modification were being developed and became more complicated in the design [33]. It contains a pair of rotaprint hollow cylindrical drums which cavities are divided into a number of smaller tanks filled with dyes. The small tanks openings on the surface of the drum are tightly closed with the capillary dyeing tips. Drawing of a fibrous bundle between such drums allows minimizing of the dye consumption and to stain thick bundles owing to the fact that the dyes are fed to them from two sides along with simultaneous squeezing of the excess staining solution.

Advantages of spraying and rotaprint methods for bringing the fibers into contact with the modifying solution are combined in the device [34] which allowed minimizing of the solution consumption, while at the same time ensuring that the fibers are completely wetted by it. The device diagram is shown in Fig. 2.6. A bundle (1) of the fibers being modified passes around the guide roller (2), rests on the support roller (3), and is supported by the motor-driven combed drum (4), which is installed in bearings mounted in the walls of the vessel (5). Airless spraying nozzle (6) is located above the

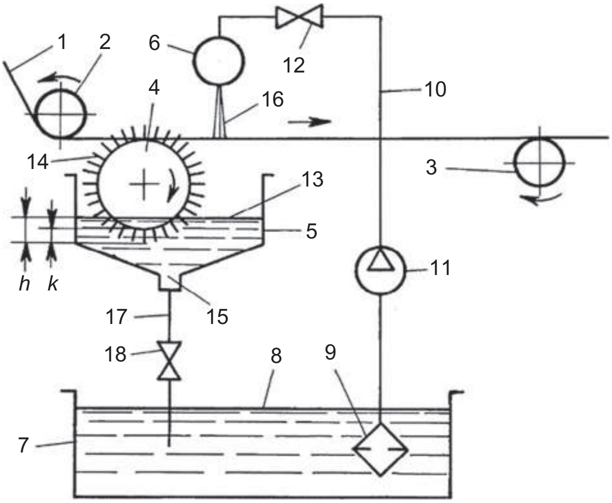

Fig. 2.6 The device for fibers modification in the process of crazing in which spraying and rotaprint methods for applying the modifying solution onto the fibers are implemented [34].

bundle (1) and vessel (5). The hydraulic unit of the device consists of a tank (7) with a modifying solution (8), a branch pipe with a filter (9) submerged into it and a piping system (10). They connect a pump (11) (via the solution flow regulator (12)) with a nozzle (6). The level (13) of the modifying solution in the vessel (5) is such that depth *h* of the drum (4) submersion into the solution is greater than height *r* of the teeth (14) of the drum: $h > r$. The vessel (5) has a drain opening (15) connected to a pipeline (17) on which a tap (18) is mounted.

The device works as follows. First, the roller system for the fiber stretching and movement is switched on; the pump (11) is then enabled. The solution (8) purified by the filter (9) is fed under pressure into the nozzle (6) and sprayed (in the form of a flare (16)) onto the upper surface of the moving bundle (1). The solution consumption in the flare is set by the regulator (12); the excess solution flows down into the vessel (5). At rotation of the combed drum (4), the fibers in the bundle (1) are pushed apart by teeth (14), thus ensuring their complete wetting, firstly, with the solution sprayed by the nozzle, and, secondly, by the drum which applies it with the rotaprint method. The drum (4) is immersed at rotation into a solution (13) and transfers it with teeth (14) and cylindrical surface onto the fibers. The solution level in the vessel (5) is regulated by a tap (18).

Fig. 2.7 shows the interaction of the bundle, combed drum, and the modifying solution. The edge of flare 16 of the solution being sprayed by the nozzle is located at distance *H* from the vertical axis of the drum (4). Length *L* of the latter is more than width *l* of the bundle of fibers $L > l$. The teeth (14) on the drum are located along its generating line in rows with angular distances α. The teeth pitch in a row equals δ. *d* is the fiber bundle thickness in front of the drum. These values are related by equation $H = K\delta^2\alpha/d$, where *K* is a dimensionless coefficient. Thus, a higher *H* value means that the teeth on the drum are more sparse and the fiber bundle is thinner. The *K* value depends on many factors: solution density; fibers and drum wetting with the solution;

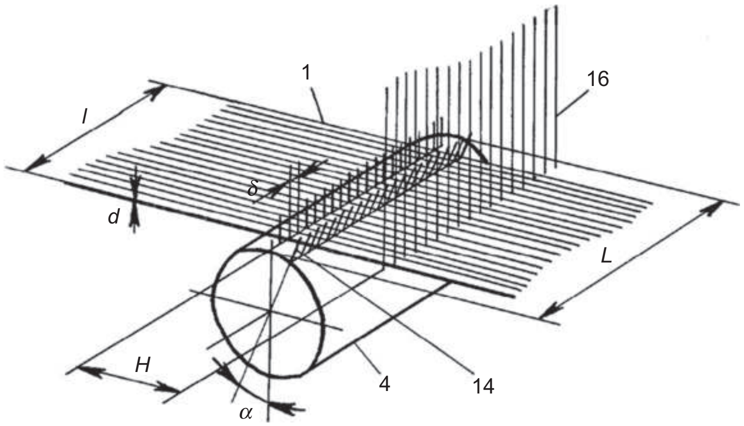

Fig. 2.7 The scheme of interaction of the device [34] components with the bundle of fibers being modified.

flow of liquid being sprayed with the nozzle; depth of the drum immersion into the solution; δ, α, d parameters; and fibers thickness.

2.3.3 Use of capillary heads

Application by means of capillary heads occurs as the result of contact of the head with the fiber by filtration through the porous material under the action of capillary forces or the excessive pressure created by the pump. The solution consumption can be adjusted by selecting capillary-porous material, changing the contact area of the head and the fiber, as well as by changing the value of hydrostatic pressure. Basic schemes of the crazing module with capillary heads are shown in Fig. 2.8. Please note the following comments.

According to Fig. 2.8A, the bundle slides in a gap between the plates in which narrow slots are made perpendicularly or obliquely to the direction of the bundle movement. The solution is pumped into the slots. In another setup, the plates have wide slots which are filled with porous material.

Fig. 2.8B envisages contact of the bundle with the capillary-porous plates submerged into baths. A constant level of the solution in the bath is maintained by overflow via a baffle. The solution is fed to the bundle (through the capillaries of the upper plate) under the pressure determined by the solution level in the bath. The solution is filtered through the lower plate under the action of capillary forces. The baths are filled with the solution from the tank (via the pump).

Fig. 2.8C is similar to Fig. 2.8A; the difference is in the form of capillary channels which are made as cylindrical openings. The contact surfaces of the plates have channels for uniform distribution of the solution across the plates' area. The openings can be filled with filtering material. The solution is fed to the heads from the tank under compressed gas pressure.

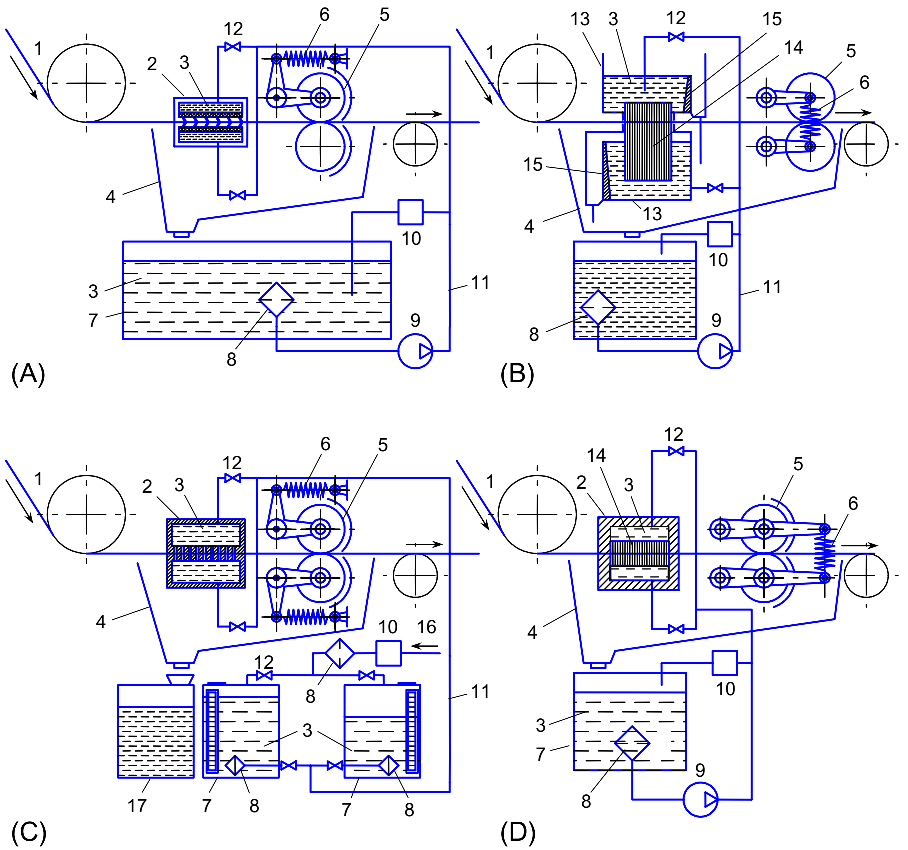

Fig. 2.8 (A–D) Applying the solution onto the fibers with capillary heads: 1—bundle; 2—plate; 3—solution; 4—tray; 5—roller; 6—spring; 7—tank; 8—filter; 9—pump; 10—pressure reducing valve; 11—liquid line; 12—flow regulator; 13—bath; 14—capillary-porous plate; 15—overflow baffle; 16—compressed gas line; and 17—accumulating unit.

According to Fig. 2.8D, capillary-porous plates serve as contact elements for both heads. The solution is pumped to the heads from the tank. Auxiliary elements of hydraulic and gas systems of the crazing module are similar to those described above.

Disadvantages of the devices for applying the modifying solution onto the fibers by means of capillary heads include:

- high probability of contamination of capillary-porous elements of the heads with solid particles and difficulty to clean them;
- complicated design of the plates containing capillary-porous elements due to the necessity for sealing the liquid; and
- limited range of filtering media with the increased wear resistance.

2.3.4 *Applying the modifying solution by watering*

A flat jet of the modifying solution, once it has come into contact with the bundle, ensures uniform distribution of the solution between fibers. This method eliminates the need for lifting devices to insert the bundle. The method is implemented by means of simple hydraulic devices, of which schemes are presented in Fig. 2.9.

Fig. 2.9A envisages that the bundle is watered with the flat jet from above. The jet is discharged from the nozzle of a special form under pressure which creates the mass of the solution available in the bath. The solution level in it is kept constant by the overflow system. The decrease in the solution level is replenished by hydraulic system equipped with a pump.

The design of Fig. 2.9B is similar to the scheme shown in Fig. 2.5B. The difference lies in the fact the solution is delivered into a gap between two rollers in the form of a flat jet. The solution's hydrostatic pressure in the nozzle is stabilized (as in the previous figure) by the excess solution overflow from the bathtub over the baffle. The rotor pump which delivers the solution into the bath is actuated with the rotating shaft of the third roller.

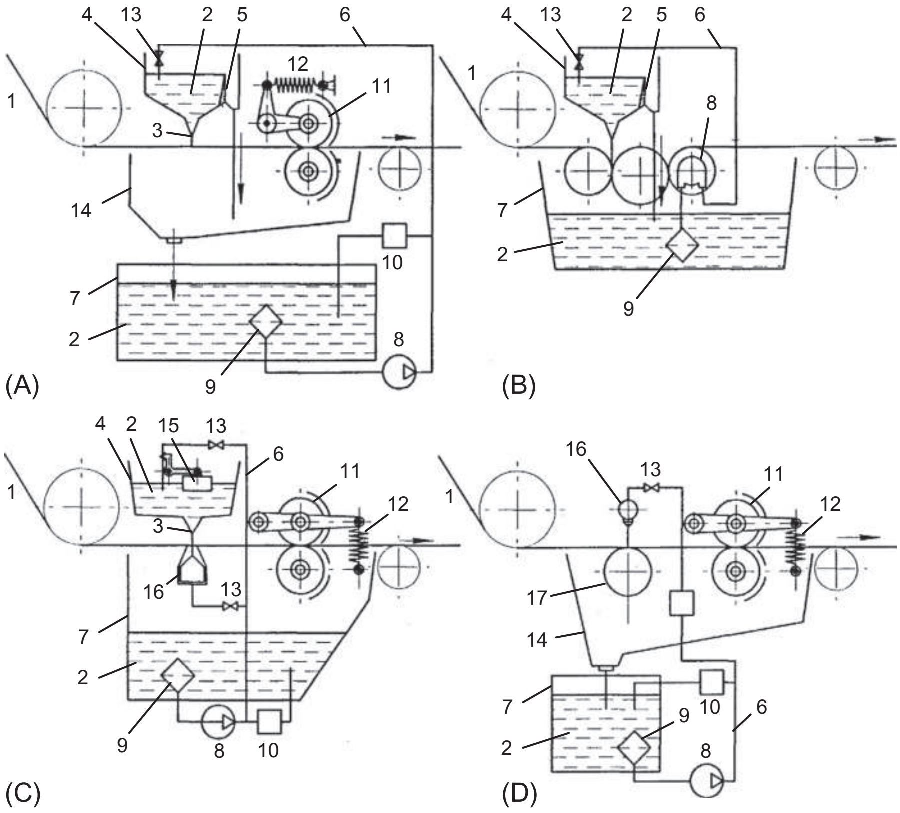

Fig. 2.9 (A–D) Watering the fibers with the flat jet of solution: 1—bundle; 2—solution; 3—nozzle; 4—bath; 5—overflow device; 6—liquid line; 7—tank; 8—pump; 9—filter; 10—pressure reducing valve; 11—roller; 12—spring; 13—flow regulator; 14—tray; 15—float-type regulator; 16—flat-slot head; and 17—supporting roller.

According to Fig. 2.9C, the bundle is watered with the solution from above and from below. The jet from above is delivered from the nozzle connected with the bath in which the solution level is adjusted by a float-type device. The bundle is watered from below with a jet from a flat-slot head connected with the pressure hydraulic system.

According to Fig. 2.9D, the flat jet of the solution is delivered to the bundle under pressure from the nozzle of the flat-slot head. The bundle is supported by the roller in place of contact with the jet. The solution is pumped into the head.

Disadvantages of the devices in which watering method is implemented include:

- nonuniform distribution of solution across the thickness of the bundle being watered according to Fig. 2.9A and B;
- complicated system to insert the bundle according to Fig. 2.9B and C;
- difficulty in synchronization of the action of oppositely directed jets of solution streams (Fig. 2.9C); and
- high-energy consumption of the solution pumping system (Fig. 2.9D).

The most obvious possibility for improving the method of processing the fibers with watering includes sealing of the area where the solution contacts the fibers. The device for continuous liquid processing of the fiber bundles [35] contains the unit with through channels along which the bundle being drawn moves. Nozzles oriented at an angle of 10–170 degrees in the direction of movement are installed in the channel walls; jets of the modifying liquid are spilled onto the bundle from these nozzles. This design simplifies the process of inserting the bundle and expands technological capabilities of modification.

2.3.5 Submersion into a bath

Fibers submersion into the solution is the simplest, safest, and an easily controllable method for wetting the fibers. The basic schemes for its implementation are presented in Fig. 2.10. They are essentially identical; the only difference is in duration of the

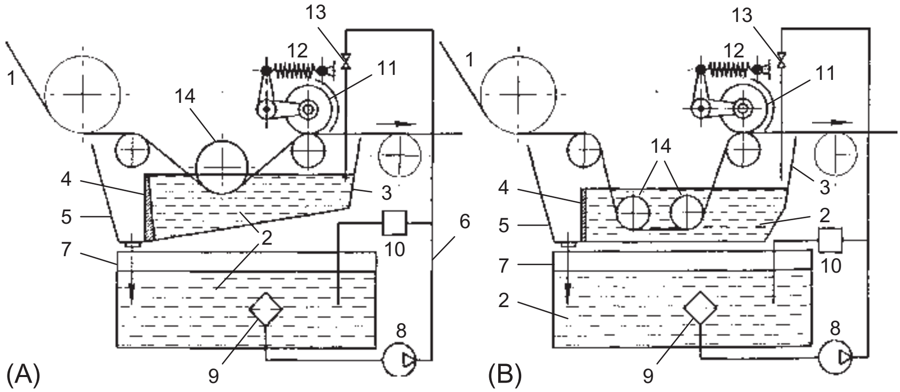

Fig. 2.10 (A, B) Applying the solution onto the fibers by submersion: 1—bundle; 2—solution; 3—bath; 4—overflow device; 5—tray; 6—pipeline; 7—tank; 8—pump; 9—filter; 10—pressure reducing valve; 11—roller; 12—spring; 13—flow regulator; and 14—immersion roller.

fibers contact with the solution. This is crucial at processing the fibrous bundles with different density of the fibers packing. Longer contact with the solution considerably improves the impregnation of dense bundles. Characteristics of the schemes are given below.

According to Fig. 2.10A, three additional rollers are installed in the line of the bundle movement and drawing which are used to submerge the bundle into the bath with the solution. The middle roller is partially immersed in the solution; its axis is above the solution level in the bath. The level is kept constant by the overflow device. A squeeze roller is installed above the third roller and rests against it.

Fig. 2.10B is similar to the previous one; the difference is in availability of a pair of rollers installed in the bath which submerge the bundle into the solution. The bundle contacts with it for a longer time, thus improving impregnation.

Both schemes include standard hydraulic systems for replenishing the baths with the solution via the pump.

Disadvantages of the method of the fibers submersion into the solution include:

- the need to seal bearing assemblies of the immersion rollers;
- the need to squeeze the bundle due to the excess solution captured by the bundle; and
- the bundle contacts the solution not at the time of the crazes initiation on the fibers (the point where the bundle leaves the guide roller), but later.

Improvement of these basic schemes offers an opportunity to resolve extraordinary tasks of modifying synthetic fibers by the method of submersion. Thus, the patent [32] protects the original design of the crazing module used to sequentially process the fibers with two solutions imparting the fibers with a complex of special properties, for example, low combustibility and biocidicity, repellent and antimicrobial activity, deodorizing and biostatic effects, etc. The device (Fig. 2.11) contains two baths, each of which is equipped with a pair of immersion rollers. In the baths there are modifying solutions I and II, which impart different functional properties to the fibers. The device also includes the hydraulic system for supplying the baths with solutions (not shown in the scheme).

Such a device is operated by the Russian JSC Vladpoliteks at production of low-combustible and fungicidal thermal and sound insulating materials for construction.

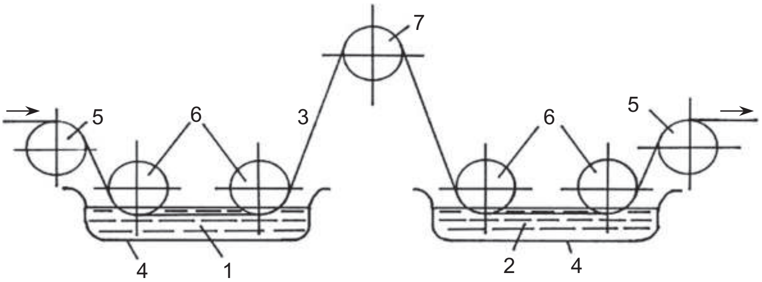

Fig. 2.11 The scheme of the device for modifying the fibers by the method of submersion into solutions of different functional purpose: 1 and 2—solutions I and II; 3—bundle; 4—bath; 5, 6, and 7—guide, immersion, and squeeze rollers.

2.4 Development of modification technique

The technology for synthetic fibers modification by the mechanism of crazing is being developed mainly with regard to improvement of the fibers drawing equipment. This is evidenced by the abovementioned patents [32–35].

The tendencies to avoid the use of inefficient heating units (like steam tube ovens) and combination of heating and drawing processes at orientational drawing of the fibers are established. In modern equipment for processing the fibers, the drawing mill rolls are differentially heated [36], drawing cylinders are equipped with electrical heating and thermal insulation [37], systems of the heated gas circulation along interconnected channels [38], and electronic units for retrieval and contactless transfer of the data on temperature distribution [39]. The process of orientational drawing of fibers is exercised under the control of computer systems which regulate heating of the drawing cylinders based on the fibers tension data [40].

The technology of introducing modifiers (transitioned to the gas phase by sublimation) into the crazes is developed. Since the evaporated particles have no solvation shell which is inevitably formed on the particles introduced into crazes according to the classic technology of crazing, their adsorption interaction with fibers increases. Advantages of the vapor-phase technology are cost-effectiveness, due to absence of wastewater, and low energy consumption [41].

Kinetic characteristics of the modifying liquid introduction into the crazes significantly increase in the field of ultrasonic vibrations. Fig. 2.12 shows the diagram of the crazing process implementation by the method of submersion with the use of ultrasound [42].

The concentrator 1 of acoustic vibrations is submerged into the modifying liquid 2 in which orientational drawing of tape (flat fiber) 3 is exercised. The end face of the concentrator is moved away from the plane of the tape for a distance of 1–5 mm. Point A of the acoustic axis crossing with the plane of the tape is within the tape portion of l_0 length on which the neck is formed; the distance between point A and the line indicating the beginning of the neck formation is $l \sim 0.5\, l_0$. Owing to that, maximum sound pressure is focused on the tape portion which corresponds to initiation and

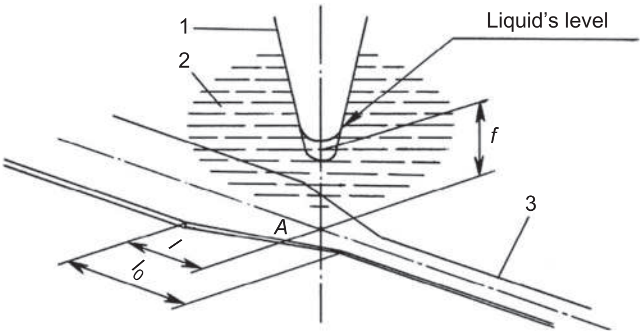

Fig. 2.12 The device for orientational drawing of polymer tapes in the process liquid [42]: 1—acoustic concentrator; 2—liquid; and 3—tape.

maximum spreading of crazes. This stipulates a higher rate of liquid penetration into the cavities of crazes and a higher concentration in them of the modifier solid particles for which the liquid serves as a carrier. By using such device, it is possible to modify fibers, threads, tapes, bundles, cords, ropes, and other long-length products made of polymers.

Development of the crazing technology for synthetic fibers modification is focused on exhaustive implementation of the following advantages:

(1) the crazing module represents a rather simple technological accessory which fits naturally into the design of the equipment used in chemical industry for orientational drawing of fibers;
(2) the crazing technology can be implemented without considerable financial expenses at the enterprises which have a line for orientational drawing;
(3) the technology allows modification of the fibers with a number of targeted additives and to impart them with a complex of special properties that significantly expand the range of application of fiber products;
(4) closed loop circulation of the modifying liquid ensures environmental friendliness of the crazing technology by creating minimum quantities of effluents as compared to the other methods of fiber modification with liquid; and
(5) the technology enables manufacturing a wide range of modified fibers in small batches, which increases flexibility of production.

A *staple machine* can be considered the basic processing equipment for industrial modification of polyester fibers by the mechanism of crazing. It is an essential piece of technological equipment for practically every enterprise producing synthetic fibers. The staple machine is used for manufacturing staple fiber, with pieces of single fine fibers 30–40 mm long being processed into the yarn on spinning machines.

A typical diagram of a staple machine is shown in Fig. 2.13. Reels with polyester fibers are put on the pins of spool rack 1. The fibers being unrolled from the reels go through the centering node 2 of the machines and are collected into the bundle which passes in sequence through three powerful drawing units (seven-roll mills).

At first, the bundle passes through the bath (3) with the oiling agent; the excess of the oiling agent is squeezed by the first drawing mill (4). Then the bundle is dried and heated in a steam chamber (5). The rotation speed of rolls of the second drawing mill (6) is higher than that of the first one; therefore, the heated bundle is subjected to

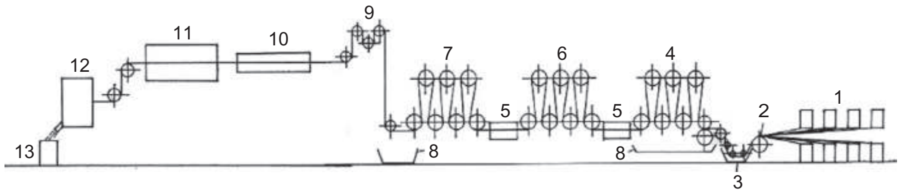

Fig. 2.13 Diagram of ShA-5 K staple machine: 1—spool rack with reels; 2—bundle forming node; 3—bath with the oiling agent; 4, 6, and 7—drawing mills; 5—chamber for the bundle processing with live steam; 8—vessel; 9—compensating device; 10—crimping machine; 11—heating chamber; 12—cutting machine; 13—area where the staple fiber is packed into bags.

the first drawing between the mills (4 and 6). After the bundle leaves the mill (6), it is heated in the second steam chamber and is drawn once again with the effort created by the drawing mill (7), which develops the highest rotation speed of rolls. The moisture condensed on the fibers after passing through the steam chambers is squeezed over the vessel (8). The squeezed-out bundle (relaxation of residual stresses in which is compensated by a device (9)) is subjected to crimping in a machine (10) to impart waviness to the fibers. Then the fiber is subjected to drying and heat setting in a chamber (11) at $T = 120–150°C$. Shrinkage of lavsan fibers in boiling water before they begin to heat set may reach 5%–7%, after heat setting—only 1%–5% [40]. The fiber is then cut in the machine (12) into staple pieces 30–70 mm long. The finished staple fiber is delivered to an area (13) where it is packed into bags.

When the bundle leaves mills (4) and (6), a neck is formed in the fibers which is a place of concentration of the crazes being initiated and growing. It is reasonable to bring this specific area into contact with the modifying liquid.

When developing the industrial technology for modification of polyester fibers by the mechanism of crazing, we strived to avoid high-cost experiments using operating equipment of the enterprises. Development of a test bench for modeling the process of orientational drawing of fibers on a staple machine was an optimal solution. The test bench enables us to refine the design and optimize working modes of the crazing unit with the modifying solutions of different nature.

Fig. 2.14 shows a design of the test bench for modeling the crazing process on the staple machine. Its main nodes are:

(1) body (1) with a set of rollers (2–4) (installed in ball bearings) to guide a bundle of fibers (5);
(2) a node for heat setting of the drawn fibers is made in the form of a pipe with stationary (6) and lifting (7) parts; it is equipped with a thermocouple (8) and current-conducting wires (9) to heater coils;
(3) a system to rewind fibers from the source (removable) reel (10) to the take-up reel (11) installed on the axis of the driving motor (both reels are fixed in bearings); the system contains the mechanism of adjustable braking and locking of the moving bundle (5) by means of a pressure roller (12) installed in a lever (13);
(4) a node for fibers submersion into the modifying liquid which is mounted on a platform (14); the node consists of a tray for a liquid (15) installed on a support (16), and rollers (17) installed on brackets and submerged into the liquid (the first of these rollers is in contact with a roller (12)); and
(5) the device control panel (18) contains the heater temperature regulator (19) (which is connected to a thermocouple (8)), a common automatic circuit breaker (20), indicating lamps (21) of activation of heating and rotation of a reel (11), switches (22) (heating), and (23) (driving motor rotation).

The test bench works as follows. Insert the bundle (5) into the rewinding system. For this, install the reel (10) with the fiber to be modified onto the axis of the corresponding bearing. Guide the bundle of fibers through the roller (2) onto rollers (17) by taking aside the pressure roller (12) using a lever (13). Lift the upper part (7) of the heater, then insert the bundle through the rollers (3 and 4) and fix it on the take-up reel (11). Close the heater. Install a tray (15) filled with the modifying liquid onto a support (16) so that the bundle-guiding rollers (17) are submerged into the liquid.

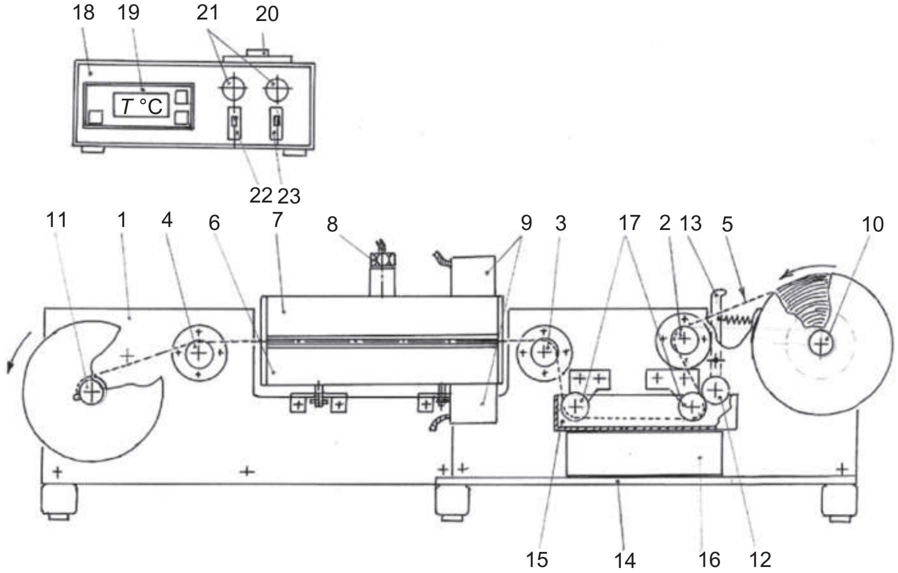

Fig. 2.14 Diagram of the test bench for fibers modifying by crazing mechanism: 1—body; 2–4—guide rollers; 5—bundle; 6 and 7—stationary and lifting parts of the heat setting unit; 8—thermocouple; 9—block of current-conducting wires to heater coils; 10 and 11—source and take-up reels; 12—pressure roller; 13—lever; 14—platform; 15—modifying liquid; 16—support; 17—immersion rollers; 18—control panel; 19—heating regulator; 20—automatic circuit breaker; 21—indicating lamps of activation of coils and reel drive 11; 22 and 23—heating and drive switches.

Activate the heating with toggle-switches (20 and 22) (a lamp (21) lights up) and set the required temperature in the pipe (6, 7) by a regulator (19). Put the reel (11) into rotation with the toggle-switch (23). Use the braking mechanism to set the required extent of a brake roller (12) pressing against the guide roller (17). This is how the draw ratio of the bundle of fibers is regulated to achieve the required rate of the crazes initiation and extent of opening in the fiber.

When the bundle passes through the rewinding system and the node for submersion into the modifying liquid (15), the source fibers stored in the reel (10) are being modified. The modified fibers are spooled onto the take-up reel (11). After the operation is finished, stop the drive and switch off the heating system from the control panel. Bring the braking mechanism into initial position and take the roller (12) away from the other roller (17) using the lever (13). Remove the support (16) and tray (15). Wipe the rollers (2, 3, 4, 12, 17).

The *crazing module* represents a technological accessory mounted on the staple machine and intended for targeted modification of the polyester fibers being processed on the unit by the mechanism of crazing. The test bench described in the previous paragraph is a prototype of the module. Specialists of JSC SvetlogorskKhimvolokno developed a set of design documentation K24-480 on the crazing module, manufactured and installed it on the staple machine ShA-5 K between the second seven-roll drawing mill and the chamber for fibers processing with live steam in the synthetic fibers workshop. Fig. 2.15 shows the scheme of the crazing module.

Reactor and modification unit are the main nodes of the device. The reactor shown in Fig. 2.16 includes a vessel (2) (capacity 150 L) installed on a platform (1). It is equipped with a system of adjustable electric heating, mixer and hydraulic pump 4 which delivers the modifying liquid to the nozzles of the modification unit.

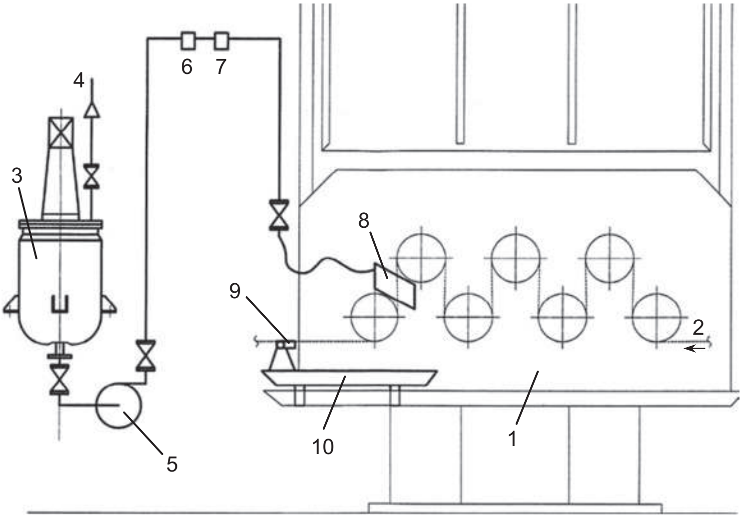

Fig. 2.15 The scheme of the crazing module and its location on the staple machine. 1—seven-roll drawing mill; 2—bundle; 3—reactor for preparing the solutions; 4—compressed air line; 5—pump; 6 and 7—filters of the first and second cleaning stages; 8—modification unit; 9—remover of the excess solution from the fibers; 10—vessel.

Fig. 2.16 Reactor: 1—platform; 2—vessel; 3—electric motor; and 4—hydraulic pump.

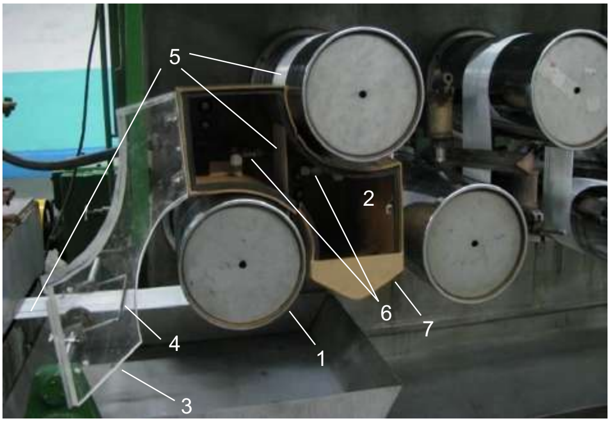

Fig. 2.17 Modification unit: 1—drawing mill rolls; 2—spraying chamber; 3—guard door; 4—squeezing clamp; 5—bundle of fibers; 6—nozzles; and 7—drain chamber.

The modification unit is shown in Fig. 2.17. It represents a spraying chamber (2) in which two spraying slot-type nozzles (6) (TEEJEET 95015 EVS) are installed. The modification unit is installed on ShA-5 K machine between the last and second-to-last (in the direction of bundle movement) rolls of the second seven-roll drawing mill. The excessive amounts of the modifying liquid are removed from the bundle with the device which contains a squeezing bracket (installed in bearings) and a vessel to collect the running-off liquid.

This simple accessory can be easily mounted on the staple machine without the need to change its setup parameters for executing a specific technological operation, and it is also easy to dismantle when the machine is operated in the standard mode. It is convenient to use the crazing module for production of small batches of fibers with tailored properties by recharging the reactor with respective solutions.

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Antimicrobial fibers

3

3.1 Problem of textile fabrics biodeterioration

"Biodeterioration" is defined as the damage of materials, raw materials, or products under the influence of biological factors [1]: microorganisms (bacteria, microfungi), insects (moths, khapra beetles, wood-boring beetles, termites, cockroaches), and mammals (rat and mice).

Materials biodeterioration can be classified into three main categories [2]: actual biodeterioration, biofouling, and biological contamination.

Actual biodeterioration takes place by two mechanisms: (1) use of organic substances by microorganisms as the source of nutrients and energy (assimilation); and (2) damage of materials caused by microbial products (destruction). Biofouling is the accumulation of aquatic organisms (bacteria, algae, sponges, etc.) on the surfaces of products. Biological contamination is the colonization of dust layers, mineral, and organic matters on hard materials' surfaces by microorganisms.

Textile fabrics biodeterioration occurs at various stages of their life cycle: in the course of fiber preliminary processing at spinning, weaving, and finishing stages due to high temperatures and humidity; during storage, transportation, and operation when the standard conditions are not met. Most of the damage caused to textile fibers occurs due to putrefactive bacteria (*Bacillus*, *Pseudomonas*, *Bacterium*) and mold fungi (*Aspergillus*, *Penicillium*, *Trichoderma*). The deteriorating effect of bacteria is due to their ability to use practically any nitrogen- and carbon-containing sources of energy and nutrients of organic and inorganic origin [3]. Biodeterioration caused by mold fungi takes place due to stress rupture of the product surface layer by the expanding mycelium in combination with a biochemical enzymatic effect. Characteristic features of biodeterioration are fabric discoloration and sheen, appearance of spots with putrefactive smell, a decrease in acid and alkali resistance and strength characteristics, loss of weight, and damage of surface layer and fibers stratification [4]. Mechanisms of textile fibers biodeterioration are determined by their origin and chemical composition.

Natural fibers are the most affected by the adverse effects of biodeterioration. Destroying agents are proteolytic enzymes (i.e., the ones that catalyze the breakdown of proteins) produced by microorganisms. Biodeterioration of wool fiber protein basis starts at pH 8.5. Ammonia accumulation in fibers leads to a pH increase, following which alkaline enzymes that are actively destroying fibers come into action [5]. Self-heating of insufficiently dry cotton and wool in the pile occurs due to intensive development of microorganisms in them. Heat energy is released when organic compounds of fibers are oxidized by waste products of aerobic bacteria. Microbiological stability of wool fibers is higher than that of cotton. Deterioration

Crazing Technology for Polyester Fibers. http://dx.doi.org/10.1016/B978-0-08-101271-0.00003-6

of wool takes place at a relatively high moisture content (over 24%), whereas development of microorganisms on cotton starts at 9% [6].

The process of synthetic fibers biodeterioration starts with adsorption of microorganisms on them. Their metabolites (intermediate products of metabolism) are diffused into the fiber micropores and cracks. The process of biological degradation is facilitated by availability of functional groups in macromolecules, weak orderliness of supramolecular structures, and low degree of polymer material crystallinity. Therefore, fibers based on heterochain polymers—polyether, polyamide, etc.—are less bioresistant. Bacterium and fungus colonies occur on lavsan on the 30th day when kept in the active microbial environment. Carbochain polymer-based fibers (chlorin and ftorlon) are more resistant to microbiological damage [7]. Biological damage of nitron, lavsan, and capron fabric causes nearly equal influence on deterioration of functional parameters of these fabrics: increasing swelling degree of the fibers by 20%–25%, reducing strength by 10%–15%, and elongation at break by 15%–20%.

Methods of textile material protection against biodeterioration are applicable at the stages of textile products handling and consumption, as well as in their manufacturing process.

The first group contains the following methods [7]:

- creation of temperature and humidity conditions for products storage and transportation under which the microorganisms lose their ability to reproduce ($T = 12$–18°C, humidity 50%–70%);
- short-term exposure to radiation and UV rays;
- purification of the air inside the warehouse;
- using ultrasound for product processing;
- airtight packaging; and
- textile products dry cleaning and washing using disinfectants.

Since these methods do not produce a long-term effect, antiseptic properties are imparted to textile materials in the manufacturing process. Antimicrobial activity of synthetic fibers is created using two groups of methods:

1. Composite methods of modification [8]:
   - polymer granulate processing with metal cations; and
   - introduction of bactericide agents into the melt or solution of fiber-forming polymeric compound.
2. Methods of surface modification [9]:
   - impregnation of fibers and threads with bactericides;
   - imparting antimicrobial properties to textile materials in the process of their dyeing and final finishing;
   - target impregnation of fabrics, knitted goods, nonwoven fabrics with solutions of antimicrobial preparations; and
   - hydrophobization of fibers' and threads' surface.

It is natural to assume that antimicrobial synthetic fibers can be manufactured using the crazing technology by introducing antiseptic substances into the crazes.

3.2 Fibers with antimicrobial properties

Products made of antimicrobial fibers have found their niche in the market of the new generation textiles. The demand for them continues to grow which has resulted in the change of priorities in textile products consumption. Therefore, the demand for fibers with antimicrobial activity has grown similarly. The demand of Western European countries in these products in 2005 amounted to 17,600 tons, and 28,000 tons in 2010. In Russia, demand is close to 15,000 tons [10].

The world's leading textile companies have been manufacturing antimicrobial chemical fibers for more than 20 years. Trevira (Germany) has developed a polyether fiber under the Trevira Bioactive brand. The antibacterial effect is achieved by volumetric chemical and physical modification of fibers that provides for long-term retention of the effect even after 100 washings. The creators of Trevira Bioactive claim that the fiber protects a person against all forms and types of bacteria, thus ensuring the purity and safety of the textile fabric. The fiber can be used in a range of applications, including production of workwear, overalls, aprons, trousers, and shirts worn by medical personnel, food industry employees, etc. [11].

The international company Nylstar (Italy) introduced bacteriostatic polyamide fibers: Meril Skinlife. These impart a long-term antiseptic effect to the textiles without causing adverse reactions to a person. Such fibers are used in production of cloths and fabrics, including medical and filter ones. The technology of antiseptic modification is based on introduction of a silver-based bactericidal agent into the surface layer [12].

Amicor, the fiber developed by Schoeller Bregenz, is considered to be an achievement in the field of bactericidal materials. This is a polyacrylonitrile fiber with antimicrobial agent triclosan. The technology of its production is a trade secret of the company. Fibers are used as a part of fabrics for production of sportswear and hosiery, as well as for production of linen and special purpose fabrics and lining materials [13].

The polypropylene fibers Prolen (manufactured by JSC Chemosvit Fibrochem) containing a silver-based bactericidal agent are intended for production of fabrics, knitted goods, and nonwoven fabrics. Textile products with the "Sanitized" logo have appeared in the European market. This mark means that antimicrobial Sanitized fibers manufactured by Clariant Co. were used in the manufacture of the product [14].

Also of interest is the Mirawave fiber, introduced by Huvis Corporation (South Korea). These polyether staple fibers have the ability to emit infrared radiation and, due to this, display long-term antibacterial activity. ABF polyether fiber suppresses the development of microorganisms owing to the bactericidal agent being part of it [15].

DAK Americas Co. has introduced the antimicrobial polyether staple fiber with the adjustable level of hygroscopicity under the "Deleron Hydro Pur" brand [12]. The fiber comprises an antibacterial agent under the trade name "Alpha San" and ion exchange resin based on zirconium and silicon phosphates containing silver, which inhibits the growth of microorganisms.

A range of products available on the Western European market of antimicrobial fibers is presented in Table 3.1.

Table 3.1 **Range of synthetic bactericidal fibers [11,12,16]**

Manufacturer	Trademark	Material fibers	Antibacterial additive
Accordis Kelheim GmbH, Germany	Danufil	Viscose	Triclosan
Lenzing AG, Austria	Lenzing Viscosa	Viscose	Silver
Montefibre SpA, Italy	Terital	PET	Silver
R. Stat SA, France	R. Stat P, R. Stat N	PET, PA	Silver
Accordis Acrylic Fibres UK Ltd	Courtek M, Amicor	PAN PAN	Triclosan
Clariant, Switzerland	Sanitized	–	Triclosan
Noble Fiber Technologies	X-Static	PA/PET	Silver
Saniwear	Terital, Leacril	PET, PAN	Silver
Kanebo	Livefresh	PA	Silver
Rhovyl	Rhovyl	PVC	Triclosan

Research institutes in Russia and Eastern Europe are also engaged in development of antimicrobial materials. The Slovak Scientific-Research Institute of Chemical Fibers has obtained polypropylene-based fibers resistant to the action of microorganisms and mold which are used in the productions of textiles and for medical purposes. The Institute of Chemical Fibers (Poland) conducts researches on the use of chitin/chitosan as additives to bactericidal fibers. Moscow State University of Design and Technology, together with the All-Russian Center of Disaster Medicine “Zaschita” (“Protection”), has developed antimicrobial materials for medical use. Katamin AB, as well as being a compound comprising potassium iodide and naphthalene sulfonate (in addition to katamin), is used as the antimicrobial agent [17].

A.N. Kosygin Moscow State Textile University, together with the Institute of Synthetic Polymeric Materials (Tver, Russia), has developed a method to impart bactericidal properties to viscose fibrous material by impregnation. Polyhexamethyleneguanidine hydrochloride (metacide), which has low toxicity, prolonged effect, and is a cationic surface-active substance (SAS), is used as the bactericidal agent [18].

JSC SvetlogorskKhimvolokno (Belarus) produces antibacterial polyether fibers containing triclosan and silver-based preparations.

In certain cases, manufacturers of antimicrobial fibers report what active additives are introduced into the polymer base, but far more often they do not provide such information, in order to protect their know-how. However, in recent years, manufacturers usually name a group of substances to which the additive belongs, to demonstrate to consumers that fibers do not contain substances hazardous to health. Since suppression of the activity of microorganisms is not a sole requirement to the antimicrobial component of synthetic fibers, it is reasonable to consider the full range of such substances and to define criteria which they should meet.

3.3 Antiseptic components of fibers

Antiseptic additives to synthetic fibers need to meet two basic requirements: suppression of growth of microorganisms, and the safety of human health. Various additional aspects of the production schedules defining technological effectiveness and consumer properties of textile products make it more difficult to meet these requirements.

3.3.1 Classification

The antimicrobial substances used in chemical industry are usually classified according to three criteria: (1) origin and chemical composition; (2) mechanism of action against microorganisms; and (3) spectrum of action.

By origin and chemical composition, antimicrobial components are divided into the following [19]:

- inorganic substances (silver, calcium, magnesium, copper compounds);
- organic compounds (nitrofuran class derivatives; benzene derivatives; 8-oxyquinolines; sulfonamide compounds; aldehydes; organic acids and their salts; SAS and compositions on their base; and
- bioorganic substances which are created by processing bacteria, fungi, plants, or their waste products (antibiotics).

By mechanism of action against microorganisms, the following substances are distinguished [20]:

- bactericidal, i.e., the ones that kill microorganisms; and
- bacteriostatic, i.e., the ones that inhibit their reproduction.

By efficiency of impact on various classes of microorganisms, antimicrobial substances are divided into groups in which a spectrum of action can be defined, as follows [21]:

- broad spectrum, if antimicrobial substances kill or inhibit a wide range of Gram-positive and Gram-negative bacteria (in 1884, Danish microbiologist H. Gram developed a method for differentiating bacteria: when stained (using the method proposed by him) cells of one type of bacteria—Gram-positive ones—get colored, while cells of other bacteria—Gram-negative ones—are decolorized);
- limited spectrum, if they are effective against certain types of Gram-positive and Gram-negative bacteria or bacteria and fungi; and
- narrow spectrum, if antimicrobial substances are active against representatives of a relatively small number of taxons of microorganisms, for example, against Gram-positive or Gram-negative bacteria.

Characteristics and a list of basic groups of antimicrobial substances used in the commodity production are given below.

3.3.2 Silver-based colloidal systems

For about a thousand years, silver has been known to be a very efficient agent against infection. However, only application of nanotechnology made it possible to obtain a long-lasting antimicrobial effect by means of silver compounds. The reason for this is as follows. Silver (in the form of metal blocks) deliver Ag^+ ions to the environment in insignificant quantities, while soluble silver salts are strong antiseptic agents which act, however, for a very short period of time. Silver particles with sizes between 10 and 30 nm provide an optimum ratio between antimicrobial activity and antiseptic effect duration. Compared to other disinfecting preparations, silver has the following advantages:

- broad spectrum of action covering about 600 microorganisms (the majority of antiseptic agents and antibiotics are active against no more than 20 microorganisms);
- high activity at low concentrations of about $5 \times 10^{-5}\,\mathrm{g\,L^{-1}}$;
- harmless to humans and warm-blooded animals; and
- long-lasting antiseptic action.

Colloidal silver is widely used to impart antiseptic properties to consumer goods made of polymer materials. A list of such products is vast and includes, for example:

- containers and sheet packaging material for foodstuffs (storage life of products in silver-containing packages increases three- to fourfold due to suppression of bacterial growth);
- products made of fiber and fabrics—e.g., surgical dressing, home fabrics, fibers for work-wear manufacturing;
- office equipment (phones, keyboards, mice); and
- hand-rails in public transport, trays, plastic lining of tables in medical premises and public catering outlets.

Silver biological activity pertains to the fact that Ag^+ ions, firstly, connect to the membrane proteins of microorganisms thus disturbing the membranes' function, and, secondly, produce solid complexes with DNA nucleotides, as a result of which DNA helical structure is broken. Both of these factors stop bacteria from reproducing.

The kinetics of microbes dying off under the antiseptic agent influence is one of its key characteristics. Die-off rate of *Escherichia coli* bacteria (colibacillus) under the influence of silver ions depends on ion concentration. So, at a concentration of $1\,\mathrm{mg\,L^{-1}}$ the colibacillus is killed in 3 min, at a concentration of $0.5\,\mathrm{mg\,L^{-1}}$ in 20 min, and at a concentration of $0.2\,\mathrm{mg\,L^{-1}}$ in 50 min. At a concentration of $0.05\,\mathrm{mg\,L^{-1}}$, it takes 2 h to obtain a complete bactericidal effect [21].

The effect of silver salts solutions is 1750 times stronger than that of carbolic acid with the same concentration, and 3.5 times stronger than that of corrosive sublimate. According to [22], antimicrobial action of silver ions is stronger than that of chlorine, chlorinated lime, sodium hypochlorite, and other strong oxidizers with the same concentration. Comparative data of disinfecting preparations are presented in Fig. 3.1 as dependences of the number of the killed bacteria Π versus time of contact t.

E. coli bacteria are more sensitive to silver ions action than *Streptococcus faecalis*. Complete inactivation (loss of activity) of *Str. faecalis* bacteria in water with concentration of 10^4 species/L occurs after 3–4 h of contact with silver solution ($0.2\,\mathrm{mg\,L^{-1}}$), while one hour is enough to suppress *E. coli* under the same conditions [23].

Besides the listed bacteria, causative agents of typhus, olm, salmonella, chromobacteria, vibrioes, causative agents of diphtheria, and other dangerous microorganisms are killed quite quickly under the influence of silver ions. It is characteristic that newly

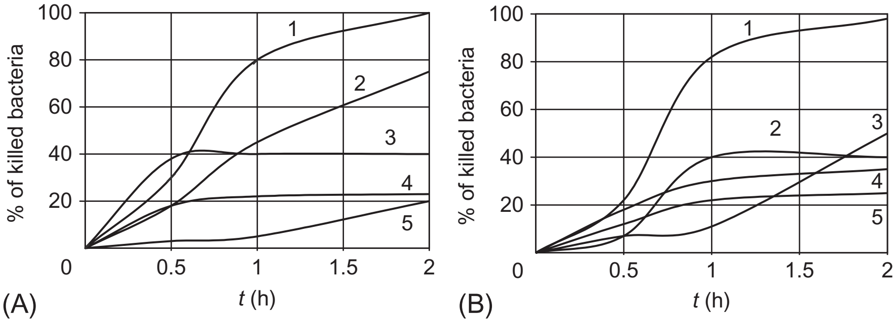


Fig. 3.1 Comparison of bactericidal action of some disinfectants against colibacillus (A) and fecal bacteria *Str. faecalis* (B): 1—silver water; 2—ammargen; 3—phenol; 4—chlorine; and 5—chlorinated lime. Reagent concentration 1 mg L^{-1}, temperature 7°C [22].

identified strains are more resistant than the old ones which are stored in a laboratory. Silver does not kill spore-forming bacteria, but spore germination in the presence of silver ions is delayed. Gram-negative bacteria are more sensitive to silver than the Gram-positive ones. Yeast and yeast-like fungi are poorly suppressed by silver. Silver has no effect on mold fungi [24]. As a rule, pathogenic (disease-producing) microorganisms are more sensitive to silver than saprophytes (organisms that feed on organic substance of dead material). Silver solution with concentration of 0.5 mg L^{-1} at temperature of 37°C and time of contact of 1–2 days deprives bacteriophages (bacterial viruses) of life.

A temperature increase reduces resistance (endurance) of microorganisms to silver. These data correspond well with the ideas on silver effect upon bacterial enzyme systems: enzymes activity decreases as temperature increases and they are more easily inactivated by inhibitors.

The bactericidal effect of silver is higher at alkaline values of pH environment. Thus, test experiments showed (at pH 8–9) a significant growth in *E. coli* bacteria, while the growth of microbes was not registered after 30 min of bacteria contact with 0.2 mg L^{-1} silver solution. At $pH < 7$, silver has no noticeable bactericidal effect on colibacillus [25].

3.3.3 Organic antimicrobial substances

At the current stage of polymer products manufacture, organic antimicrobial substances are becoming more effective than inorganic ones thereby forcing the latter out of the market. By chemical nature, the following groups of antimicrobial additives used in polymer materials are distinguished [26,27].

Aldehydes, organic acids and their derivatives. *Salicylanilide* is a colorless and odorless crystal powder; soluble in alcohols, ethers, and benzene; poorly soluble in water; $T_m \approx 136$–138°C; used as a fungicide (agent that destroys or suppresses pathogenic fungi) for nonmetallic materials and as an antiseptic agent in production of film materials and artificial leather. *Methoxyacetaldehyde*, which is used as the antimicrobial plastics modifier, is soluble in water, alcohol, and acetone, less soluble in ether;

possesses a sweet taste; $T_b = 92.3$°C. *Benzoic acid* is a white crystal powder having a characteristic odor; poorly soluble in water, freely soluble in alcohol, ether, and benzene; $T_m = 122.3$°C, $T_b = 249.2$°C; it is an antiseptic and preservative agent used in production of dyes, medicines, and fragrances. *Sodium benzoate* has long been known as a preservative agent, stabilizer for polymers and corrosion inhibitor; it is a crystal powder that is soluble in water and alcohol. *Copper naphthenate* (technical product) is a greenish-blue pasty substance; insoluble in water; marginally soluble in organic solvents; fungicide, antiseptic agent for wood, ropes, and fabrics. *Magnesium acetate* is a crystal substance; soluble in water, methanol; $T_m = 323$°C (with decomposition); deodorizing, antiseptic, and disinfecting agent; main field of application: disposable nonwoven products (napkins, towels).

SAS and SAS-based compositions. Cationic antimicrobial agent *Katamin AB* is a colorless or yellow transparent liquid; soluble in water; used to disinfect fabrics, surfaces of metal and wooden products; can be introduced into a cement mix. *Althosan MB* is a transparent colorless liquid; soluble in water; used as a bactericide, deemulsification agent, and corrosion inhibitor; it has a wide range of antimicrobial activities. *Katapins* are brown liquids or salvy substances; soluble in water, alcohols, and benzene; insoluble in ethers; used as corrosion inhibitors, broad-spectrum antimicrobial agents, wetting agents, and emulsifiers.

Compound ethers, phenols and their derivatives. The most common *parabens* (paraben acid derivatives) are *methylparaben* and *propylparaben*—white or yellowish crystal substances with a faint specific ("phenolic") odor; they are soluble in alcohols, partially soluble in water; they are used as preservatives in cosmetics [28]. *Triclosan* is a white color powder with a faint pleasant odor; poorly soluble in water, freely soluble in alcohols, organic solvents; $T_m \approx 55–60$°C, is used as a broad-spectrum antimicrobial component for a large number of cosmetics and perfumery products [29].

Other antimicrobial substances. In recent decades, a new class of substances—water-soluble polymers (polyguanidines) with broad-range and stability of antimicrobial action and low toxicity—has occupied its niche within the biocides market [30]. *Metacide* is a salvy substance of light yellow color, odorless, soluble in water and organic solvents; it is a typical representative of substances of this class. It is used to impart antimicrobial activity to genuine leather, paint coatings, and products made of polymer materials. Polyguanidines are a part of antiseptic agents allowed for household use (*Inkrasept*). *Copper 8-oxyquinolate* (Cuprocin) is used to protect fabrics, paper, wood, paints, and plastics against microbial damage.

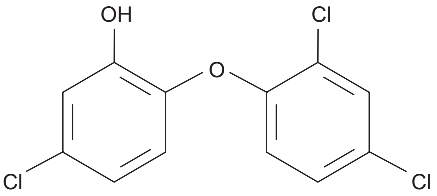
According to hygienic classification, all listed antimicrobial substances are related to Class 3 (moderately hazardous) and Class 4 (slightly hazardous). For example, LD_{50} indicator (a lethal dose which causes the death of 50% of a group of test animals, in grams per kilogram of animal body weight) for methyl- and propylparabens is about $8\,g\,kg^{-1}$; benzoic acid—$1.7\,g\,kg^{-1}$; salicylic acid—$0.89\,g\,kg^{-1}$ [28]; triclosan—$4.3\,g\,kg^{-1}$; values for polyguanidines are within the range 0.2–$0.4\,g\,kg^{-1}$ [25].

The analysis of the list of antimicrobial agents used by modern industry has led to the following conclusion. Triclosan and colloidal silver solutions are best suitable for use (by criteria of antimicrobial activity, safety to human health and technological effectiveness) as basic biocides for polyethylene terephthalate (PET) fibers modification using the crazing technology. The development of modifying compounds based on these substances is addressed in the following sections.

3.4 Modifying compounds based on triclosan

The main problem of triclosan (Tr) introduction into the crazes is considerable viscosity of its solutions and their poor wetting of PET fibers. Attempts to overcome this challenge by Tr dissolution in alcohols and other organic solvents results in the occurrence of many other problems. It seemed like an optimum solution to substitute Tr true solutions with its aqueous suspensions. Water is much cheaper than solvents that are irrecoverably lost in the production process, is compatible with PET fibers oiling agents, and is environmentally safe. Actually, the development of stable surface-active Tr aqueous suspensions has determined the competitiveness of antimicrobial PET fibers obtained by the mechanism of crazing.

Triclosan is a substituted diphenyl ether; to be more precise, it is 2,4,4-trichlor-2-hydroxydiphenyl ether with the molecular weight of 289.5. Its structural formula is as follows.



Tr was developed in the 1960s as a broad-spectrum antibacterial agent. Its developer—the Ciba-Geigy company—has become its main supplier to the world market. At first, Tr was believed to be a nonspecific antiseptic agent destroying any cells. Soon it was established that Tr has a selective effect on microorganisms by primarily suppressing prokaryotes—bacteria that lack a membrane-bound nucleus and typical chromosomal apparatus. The majority of pathogenic bacteria are prokaryotes. Twenty years of clinical tests and accumulation of facts have led to the conclusion that Tr is effective in small doses, has a broad spectrum of action and no negative effects on human health and the environment, which distinguishes it favorably from the majority of antimicrobial agents [31].

According to the data provided by of F.F. Erisman Federal Scientific Center of Hygiene (Table 3.2 [29]), Tr is active against the majority of pathogenic microorganisms settling on the skin's surface.

Tr's importance as a broad-spectrum antibacterial agent is confirmed by the practice of intrahospital infections suppression with its help [32]. In addition, Tr has antiinflammatory effect [33] by blocking synthesis of inflammatory mediators in fibroblasts (main cellular form of connective tissue) and suppressing the eukaryotic cells, which initiate inflammation.

Table 3.2 **Microorganisms which growth is suppressed by triclosan**

Gram-positive bacteria	Gram-negative bacteria	Fungi and yeast microorganisms
Staphylococcus aureus *Staphylococcus epidermidis* *Streptococcus pyogenes* *Propionibacterium acnes* *Clostridium tetani* *Corynebacterium species* *Salmonella paratyphi A, B* *Salmonella choleraesuis* *Shigella flexneri* *Shigella dysenteriae* *Vibrio cholerae*	*Escherichia coli* *Enterobacter cloacal* *Enterobacter aerogenes* *Klebsiella pneumoniae* *Proteus vulgaris* *Proteus mirabilis*	*Candida albicans* *Epidermophyton floccosum* *Trichophyton mentagrophytes* *Tricophyton rumbum*

Thus, the safety criterion has become a primary argument in selecting Tr (other conditions being equal) as the antimicrobial component for PET fibers. Tr's biocompatibility is confirmed by the results of numerous laboratory, toxicological, and long-term clinical trials.

Tr water emulsions were prepared using the surface-active components to stabilize the thermodynamically unstable suspension of Tr microdrops in water. It seemed feasible to use for this purpose the substances that are part of the process liquids, ensuring the oiling effect at PET fibers processing.

Sintezin was the first investigated substance of this group. The main characteristics of sintezin 41–82—a commercial product purchased by chemical industry enterprises—are presented in Table 3.3.

The modifying emulsion preparation process consists of three operations: (1) Tr dissolving in alcohol; (2) preparing the sintezin aqueous solution—mixing the sintezin in one-third of the total amount of water, heating the mix to 50°C, adding the remaining water while stirring; and (3) mixing the first and second solutions using a high-speed mixer. A suspension with the smallest particles (diameter ~ 1 mcm, determined by an optical microscope) is received when using the following ratio of components (% by mass): Tr—1, sintezin—1, ethyl alcohol—30, distilled water—68.

The emulsion thus obtained has a pronounced antimicrobial activity. At microbiological testing, a zone (7–8 mm wide) of suppression of growth of microorganisms being tested is formed around the emulsion drop specimen on an agar plate (Fig. 3.2).

Table 3.3 **Sintezin 41–82 technical data**

Parameter description	Value
Appearance	White color paste
Water content (% by mass), no more than	42–46
pH of an aqueous solution of 10% by mass	7.5–8.5

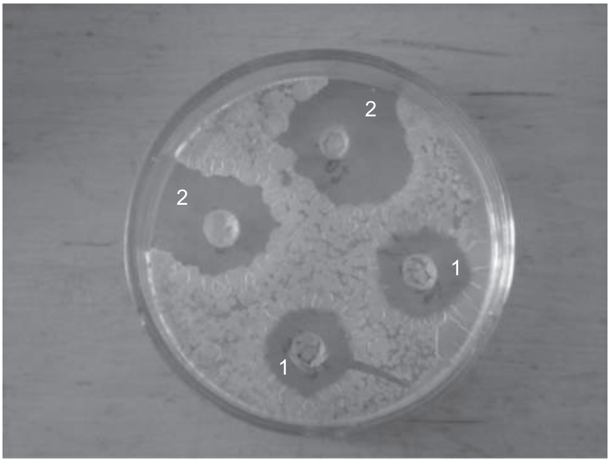


Fig. 3.2 Petri cup inhabited with *Staphylococcus*-type bacteria with antimicrobial emulsion samples: 1—with sintezin and 2—with sintanol.

In the course of bench tests an essential drawback of such modifiers was revealed: stratification of the mix and settling out of crystals occur in approximately 5 h after preparation of the solution. It is conceivable that stratification is caused by physical and chemical bonding of alcohol and sintezin molecules, resulting in depletion of Tr solution with solvent.

The analysis of IR absorption spectra of the mixture components presented in Fig. 3.3 (Fourier IR-spectrophotometer NICOLET 5700) gives evidence of a more complex mechanism of their interaction. It is apparent that the settled-out product is not Tr crystals, but rather a complex combination of Tr and sintezin. Spectrum 3 has absorption bands which are characteristic for Tr in the range $\nu = 3000–3500\,\mathrm{cm}^{-1}$, peak at 1880, double peak at 1600, and a group of peaks in $800–1600\,\mathrm{cm}^{-1}$ range. At the same time, spectrum 3 is more "diffused" as compared to spectrum 1 and contains peaks inherent to sintezin at $\nu = 2800$ and $2930\,\mathrm{cm}^{-1}$. It is natural that such a modifier is inconvenient for technological operations at continuous production lines, which should ensure time-stable antimicrobial effect.

Sintanol is SAS used in standard compositions of oiling agents for PET fibers (individually or in the mix with sintezin). Sintanol DC-10 manufactured by Hoechst (Germany) is a mix of polyethylene glycol monoalkyl ethers based on primary fatty alcohols $C_nH_{2n+1}O(C_2H_4O)_mH$, where $n = 10–18$, $m = 8–10$. Experiments on Tr water emulsions preparation using this substance were held by controlling IR spectra of the received products. They give evidence of physical and chemical interaction between emulsion components which, most likely, results in Tr microdrops stabilization by creating (on their surface) a structural and mechanical barrier against nonionic molecules of sintanol [34]. Particles of such microemulsion are characterized by a very low surface tension at the boundary of water [30]. The following

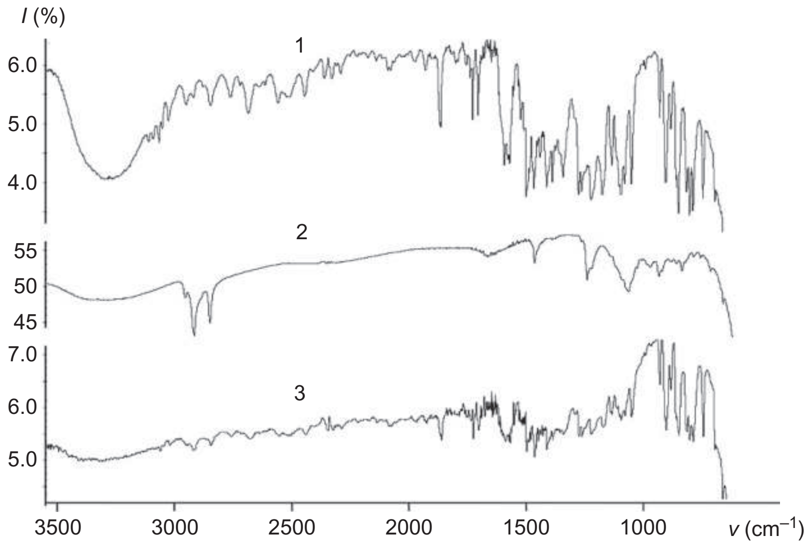


Fig. 3.3 IR absorption spectra: 1—Tr; 2—sintezin; and 3—settled-out product.

composition of Tr emulsion [35,36] (% by mass) has been developed to implement the crazing technology for obtaining antimicrobial PET fibers:

Triclosan	0.8–1.0
Sintanol	3.0–4.0
Distilled water	95.0–96.2

Neonol is another surface-active component of oiling agents for polyether fibers. It is a polyethylene glycol monoalkyl ether based on secondary fatty alcohols $(C_nH_{2n+1})(C_mH_{2m+1})CHO(C_2H_4O)_pH$, where $n+m=10–20$, $p=12$. A modifying compound for PET fibers is prepared using neonol aqueous solution in which Tr is dissolved. Optimum compound composition is as follows (% by mass): Tr 1.0–1.5; neonol 3.0; distilled water 95.5–96.0. This compound is surface active and PET fibers drawing in it is accompanied with intensive crazes formation. Crazes are filled with the liquid phase which retains antimicrobial activity inherent to Tr [37].

In conclusion, it should be noted that the optimum area of triclosan utilization in the crazing technologies for synthetic fibers modification is the creation of its emulsions in aqueous environments possessing surface activity.

3.5 Modifying compounds containing silver

The introduction of silver and compounds based thereof to the fibers' structure results, along with clear benefits (bactericidal action, lack of skin irritant effects, long-term antimicrobial effect), in a significant increase in the price of fibers (the cost of precious metal additives is added to the fibers price). The expediency of, firstly, modifying the fibers' surface layer only to avoid "trapping" of silver particles in polymer matrix, and, secondly, using colloidal, preferably nanodimensional silver particles, in the modifying compounds to maximize area of their contact with the microbial environment is evident. These problems can be solved rather simply through introduction of silver to the fibers structure by the mechanism of crazing.

Antiseptic compounds for fibers processing should address the following issues. Firstly, acceptable balance between the basic level of the modifying fibers antibacterial activity and duration of their antiseptic action shall be ensured. Secondly, mandatory retention of antimicrobial effect when washing the modified-fibers-containing textile products shall be ensured. These requirements are inconsistent and therefore creation of antiseptic compositions demanded the structure optimization and development of nonstandard methods for their preparation. It is obvious that fibers with high silver ions concentration on the surface will have the greatest antiseptic activity. However in this case the duration of silver action is small, as ions of metal will leave the fiber surface layer within a relatively short service life of a textile product.

Optimization of the structure and mechanism of action of a silver-containing modifier of fibers by the "activity/duration of action" criterion can be carried out observing several technological principles, the most significant of which are the following.

1. Use of silver particles in colloidal or nanodimensional range. There is a known chemical phenomenon according to which solubility of solid particles in liquids is inversely proportional to the radius of curvature of the particle. The degree of solubility (concentration of a saturated solution) and the rate of colloidal particles dissolution increase as they approach nanodispersion state due to increase in the total particles surface area.
2. Use of slightly soluble antiseptic compounds. By selecting solid substances which have different solubilities and by varying the size of their particles, it is possible to find the required optimal ratio between activity and duration.
3. Immobilization (fixation) of silver ions by the fibers polymer matrix containing functional groups which bind the ions.

When carrying out the work, all aforementioned methods were used.

The main task was to stabilize the colloidal silver solutions. Success in addressing the problem has ensured technological effectiveness of crazing processing and constancy of fiber properties. Preliminary experiments showed that ideally the metal colloidal solutions intended for fiber modification should meet the following requirements:

- optimum particle size—10–50 nm;
- resistance to conglomerates formation;
- resistance to sedimentation (settlement);
- stable adhesion of particles to polyether polymers; and
- colloidal solution compatibility with components of textile-processing chemicals.

When developing the modifying compounds, a focus was placed on reduction of silver concentration in compositions and compensation of its shortage by introducing less expensive antiseptic agents into the compound. The latter were selected in such way so that they could carry out additional functions of colloidal particles stabilizers in compounds.

3.5.1 Cultivation of silver nanoparticles

The idea of obtaining silver-based modifying compounds was to cultivate silver nanoparticles in an aqueous stock solution.

The simplest way to implement this idea is chemical reduction of silver salicylate (water-insoluble silver salt of salicylic acid $C_6H_4(OH)COOAg$ in aqueous solution of ethylene glycol). The formed silver particles (average size 10–50 nm, mass concentration 1.5%–3.0%) are stabilized due to the presence of polyvinyl alcohol (PVA) and SAS—micro-crazing initiators—in the solution. At crazing processing of PET fibers with this compound, silver nanoparticles are glued by ethylene glycol (PET plasticizer) to the walls of crazes and fiber surfaces. A PVA film covers the glued particles and ensures the prolonged silver ions discharge into a wet environment [38].

Formation of silver particles directly in the crazes allows a considerable reduction in silver processing losses. For this, a modifying aqueous compound is used which contains the following: silver salicylate dispersion; neonol—a component of an oiling agent for fibers; cetylpyridinium nitrate—cationic SAS, bactericide; and freely-soluble-in-water sucrose, α-D-glucopyranosyl-β-D-fructofuranoside. Components of the compound (which has entered the crazes) physically and chemically interact when the fibers are passing through a steam chamber.

At $T = 100$–150°C, silver salicylate is reduced by the sucrose aldehydic group to metal silver. The nitrogen-containing pyridinium group possesses strong affinity to silver and is adsorbed on its particles, and hydrocarbon “tails” of cetylpyridinium molecules impart hydrophobic properties to silver particles. Neonol molecules stabilize the “tails.” Thus: (1) colloidal silver particles are formed in the crazes; (2) heat treatment of fibers in the steam chamber serve two functions—thermofixation of the oriented structure of fibers and initiation of the reaction of silver reduction from salicylate; and (3) neonol and cetylpyridinium determine the crazes formation and stabilization of colloidal silver particles which are formed in the crazes [39].

An increase of colloidal stability of the modifying compounds is an actual task of the crazing technology. It was solved by formation (in the compositions) of complex compounds consisting of silver ions and products of sucrose polycondensation. For this, a mix of silver nitrate $AgNO_3$ and sucrose diluted with water was heated to 110–120°C. A change of color of the mass to yellow-brown meant that dehydration and sucrose polycondensation took place. It was diluted with water, then glycerin was added—triatomic alcohol $CH_2OH–CHOH–CH_2OH$ acting in the composition as a solvent, “soft” reducer of silver ions and viscosity controller. The procedure of silver ions reduction consists of thermostatic control of the mixture at 80–90°C. The formed nanoparticles are stabilized by the sucrose polycondensates. The composition of an antiseptic modifier of PET fibers, which is optimal by the criterion of colloidal stability, is as follows (% by mass): silver 1.5–3.0; polysucrose 1.5–3.0; glycerin 8.0–12.0; water—the rest [40].

3.5.2 Cultivation of bimetallic particles

When applying technologies envisaging the use of precious metals, the problem of reducing the consumption of the latter is always of crucial importance. A task was set to reduce silver concentration in the modifying compound by adding another, cheaper metal which creates antiseptic effect. It was solved by cultivation of colloidal copper particles on which surface the nanodimensional silver particles are settled.

The methodology of obtaining modifying compounds with bimetallic particles is as follows. When a colloidal copper solution is added to the silver nitrate solution, copper particles serve as a silver ions reducer by the exchange reaction mechanism:

$$2Ag^{+} + Cu = Ag + Cu^{2+}$$

Bimetallic particles demonstrate complex antiseptic action: silver—against fungi, bacteria, and viruses; copper—predominantly against fungi, especially mold ones. Exchange reaction of ions reduction prevents formation of silver dendrites as the growth of silver particles is localized at the centers of reduction and is limited by the size of colloidal copper particles.

The method of obtaining a modifying compound with bimetallic particles from the mix of silver nitrate and copper acetate $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solutions is offered [41,42]. Reduction of Ag^+ ions takes place as the result of interaction of silver nitrate with the equimolar amount of sodium borohydride ($NaBH_4$ sodium tetrahydroborate) in hydroglyceric solution:

$$AgNO_3 + NaBH_4 + 3H_2O = Ag + H_3BO_3 + NaNO_3 + 3.5H_2$$

The reaction of copper particles reduction by borohydride from the copper nitrate solution is performed in similar manner, but with a larger yield.

For stabilization of the formed bimetallic particles, 0.1%–0.2% cetylpyridinium chloride ($C_{12}H_{36}NCl$—cationic SAS used in production of bactericidal detergents) is added to the mix. It serves two functions: metal particles stabilizer and antiseptic agent. Antimicrobial action of the compound is enhanced by the boric acid which is formed at reduction of silver and copper ions.

This method has been improved to increase the colloidal stability of the modifying compound. It has become possible to considerably reduce the probability of metal particles sedimentation through the use of the stock dispersion medium in which colloidal chemical reactions of metals reduction take place. It represents an aqueous solution of glucose ($C_6H_{12}O_6$—carbohydrate containing aldehyde and alcohol groups), glycerin, and cetylpyridinium chloride. Glycerin and glucose are reducers of Ag^+ and Cu^{2+} ions and the solution viscosity regulators. Due to the inequality of their oxidation-reduction potentials, the process of silver and copper reduction in glycerin-glucose aqueous solution proceeds more evenly in time.

Silver nitrate, copper acetate $Cu(CH_3COO)_2{\cdot}1.5H_2O$ and sodium borohydride are dissolved separately in the stock medium. Mixing of these components sets optimum sequence of chemical reactions of the compound synthesis.

First, the reaction of copper ions reduction is performed, which is generally described by the equation:

$$Cu\left(CH_3COO\right)_2 + 2NaBH_4 + 6H_2O = Cu + 2H_3BO_3 + 2NaCH_3COO + 7H_2$$

It is accompanied by a release of hydrogen and a change of the solution color from blue-green to green-brown. Colloidal copper particles are stabilized at the time of formation (*in statu nascendi*) due to adsorption of cetylpyridinium ions. The increased viscosity of the glycerin-glucose stock medium makes the formed colloidal system stable.

The colloidal copper solution thus obtained is mixed with the silver nitrate solution in stock medium to initiate the aforementioned exchange reaction for silver ions reduction. The remaining Ag^+ ions are reduced by the glucose if the mixture is heated above 50°C. At the same time ions of bivalent copper Cu^{2+} are reduced to monovalent copper which forms oligomerous complex compounds with glucose oxidates and glycerin. Polar oligomerous complexes are adsorbed on metal particles, thus stabilizing them.

By means of the instrument [43] it is established that all compounds mentioned in Sections 3.4 and 3.5 initiate craze formation.

3.6 Antimicrobial activity of fibers

Efficiency of the developed compounds as the technological medium which imparts antiseptic properties to polyether fibers is assessed by processing the fibers by the mechanism of crazing at the stand described in Section 2.4 (Fig. 2.14). Experimental samples of antiseptic fibers were subjected to microbiological trials. Then, a pilot batch of antimicrobial PET fibers was produced using the industrial equipment; microbiological characteristics and feasibility of their inclusion into the structure of antiseptic textiles were determined.

3.6.1 Antimicrobial fibers production

Experimental samples of active fibers were produced using PET fibers with a linear density of 0.84 tex (manufacturer JSC Mogilevkhimvolokno). The stress-strain characteristics of such fibers determined using Instron 5567 tensile tester at stretching speed of 50 mm min^{-1} are presented in Fig. 3.4.

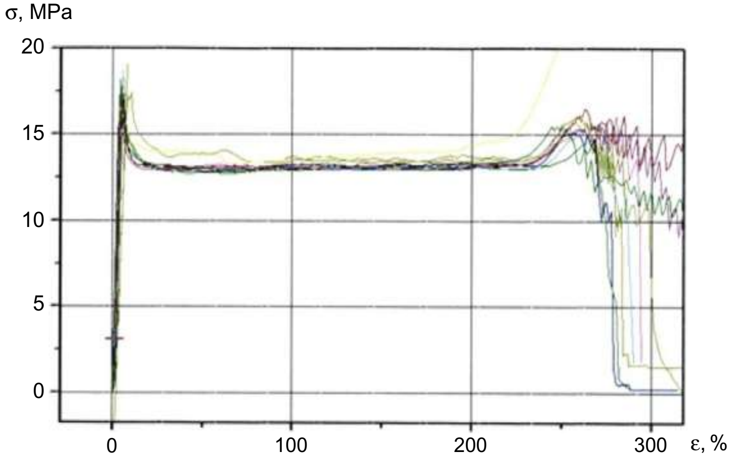


Fig. 3.4 Stress-strain curve for a bundle of initial PET fibers.

The analysis of dependences $\sigma(\varepsilon)$ shows that at the initial stage of stretching the fibers are elastically deformed and the stress in them reaches its maximum value $\sigma = 18–19$ MPa at relative elongation $\varepsilon \approx 15\%$. Then the stress exponentially decreases since a neck is formed on the fibers and the crazes (which quickly grow in number) appear on it. At $\varepsilon \approx 20\%$, the crazes start to spread and the fibers demonstrate forced elasticity. During the shear flow which continues until $\varepsilon \approx 230\%$ a fibrillar structure is formed in the fibers. Stretching of fibrils results in the increase of stress in the fibers to $\sigma \approx 17$ MPa. Then the process of fibrils rupture takes place in the elongations interval $\varepsilon \approx 280\%–300\%$, since the stress in a bundle of fibers and in an individual fiber consisting of fibrils is distributed unevenly.

The stage of maximum spreading of the crazes is the most favorable for introduction of antiseptic compositions into the structure of such fibers. It comes after achieving σ, which corresponds to elongation $\varepsilon = 200\%–230\%$, and continues until the fibers start to rupture.

Experimental samples are produced at the stand with the fibers draw ratio $\varepsilon = 210\%–230\%$. The temperature of the modifying compounds amounted to 20 ± 1°C, thermofixation temperature 98°C, fibers drying temperature 90°C.

A pilot batch of antimicrobial fibers was manufactured by JSC “SvetlogorskKhimvolokno.” Freshly formed PET fibers manufactured at this enterprise (type 3, linear density of 0.44 tex) were used as source material. Their stress-strain characteristics were determined using Textechno H. Stein 41066 tensile tester. These fibers, as compared to the ones manufactured in Mogilev, have lower strength ($\sigma_{\text{B}} \approx 4–5$ MPa) and lower relative elongation at rupture. Analysis of charts $\sigma(\varepsilon)$ resulted in establishment of optimal modes for their crazing processing.

The fibers were manufactured in a weaving and spinning shop at a staple machine ShA-5K equipped with the crazing module (see Figs. 2.15 and 2.17). Ninety-nine reels of fiber were loaded on a bobbin carrier, and a weighed amount of a bundle of initial fiber was 74 g m^{-1}. Pressure of the modifying compound supply to the nozzles was kept constant, at 3.5 MPa, and flow rate was regulated within 0.3–1.6 L min^{-1} depending on wetting of the bundle and volume of the excess liquid returning to the circulation line. The temperature in the chambers for oriented fibers fixation was $T = 98.5$°C. Thermoset fibers were crimped (number of crimps per 1 cm length—not <3), cut into pieces of 65 ± 10 mm length and brought into the drying chamber with $T = 125–135$°C.

Bactericidal and bacteriostatic fibers were manufactured as a part of the pilot batch. Bactericidal fibers (from *bacterium* and the Latin *caedo*, meaning “I kill”) are fibers that are capable of killing bacteria, and bacteriostatic fibers (from *bacterium* and Greek *staticos*, meaning “static, motionless, fixed”) do not upset the balance of bacteria on the skin, but temporarily stop bacteria from reproducing.

Bactericidal fibers were obtained by using the modifying compound with triclosan and sintanol. The composition was prepared as follows [35]: sintanol was diluted upon stirring in a small volume of water warmed up to 50°C, then triclosan batches were added and the solution was diluted with the remaining water. Bactericidal fibers production was carried out at the bundle speed of 16.1 m min^{-1} and draw ratio of 210%, and the temperature of the modifying compound amounted to 28°C.

Bacteriostatic fibers were processed with the compound based on triclosan and sintanol in which the triclosan concentration was reduced twofold and a solution of colloidal silver (Adjetta trademark) in the amount of 4% by mass was additionally introduced. The composition was prepared similarly to the previous one, then the Adjetta solution was added in batches to the mix. Fibers of the pilot batch were manufactured with a speed of 13.6 m min^{-1}, a draw ratio of 230%, and a modifier temperature of 26°C.

A specific feature of triclosan aqueous solutions lies in the fact that stirring can cause foam formation. This disadvantage can be eliminated by adding (into the concentrated solution) a small amount of an antifoaming agent before dilution with water: 10 mg/100 kg of the diluted solution.

The technological modes for antiseptic compositions preparation, as well as for obtaining the bactericidal and bacteriostatic PET fibers are regulated by enterprise standards [44].

The industrial batch (about 500 kg) of bactericidal PET fibers modified by the compound based on triclosan [37] was manufactured on the test installation for staple fiber processing at JSC Mogilevkhimvolokno. Under the control of the Center of Scientific Research in the Light Industry (Minsk, Belarus), the manufactured fibers were used in the textiles industrial production at Belarus enterprises: JSC Kobrin Spinning and Weaving Mill Ruchaika, JSC Gronitex, and JSC Polesye. The antimicrobial fibers batch was processed on the standard equipment into cotton-polyether yarn (260 kg) at JSC Gronitex (Grodno). It met the requirements to the yarn, grade 1, according to Belarus standard specification 500046539.055–2002. At JSC Bobruysktrikotazh, a pilot batch of plush cloth for bedsheets was made of the antimicrobial yarn [45].

3.6.2 Methods of antimicrobial fibers testing

Primary microbiological control of fibers and fabrics made thereof (initial and subjected to washing) was carried out with respect to testing cultures of *Staphylococcus aureus*, *Staphylococcus epidermis*, and *Pseudomonas aeruginosa* bacteria which simulate pathogenic microflora of human beings. The testing cultures are grown from the certified strains stored in the collections of the Institute of Forest of NAS of Belarus and Gomel Regional Center of Hygiene and Epidemiology.

The standard methods for assessment of the textile fibers antimicrobial effect are developed in many countries. The fibers antiseptic properties were determined using the methodology which summarized the essential features of similar purpose standards: AATCC 100-1993 (USA), SN 195924-1983 (Switzerland), and JIS 1902-1998 (Japan).

Cultures of microorganisms were sowed in Petri cups with the agarized nutritive medium. A sample of modified fibers (~0.03 g) was placed into the cup. The cups with samples were kept in a thermostat at temperature of 29 ± 2°C and relative humidity in air of 90% during 14 days. Width h of a zone of suppression of bacterial growth around the sample was registered according to the Russian State Standard (GOST) 9.802-84. The basics of the method are explained in Fig. 3.5 [45], where it can be seen that the biofilm of testing bacteria *S. epidermis* has grown to the edges of the sample from the initial PET fibers (Fig. 3.5A), but has not entered the zones of bacterial growth suppression which are forming round the fibers and which had been processed by the colloidal silver solution (Fig. 3.5B) and triclosan (Fig. 3.5C).

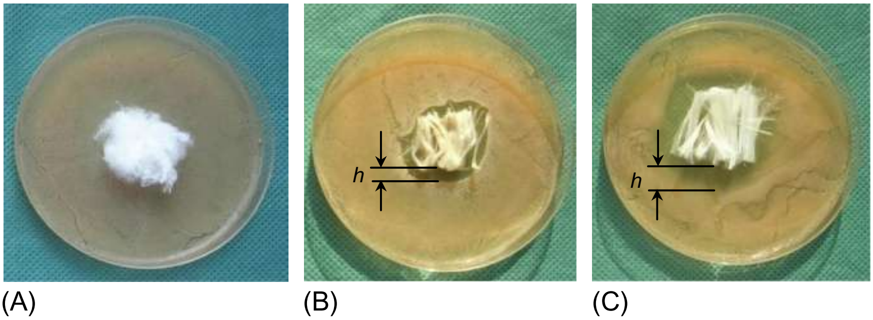


Fig. 3.5 Suppression of growth of testing bacteria *S. epidermis* by PET fibers: (A) initial fibers, (B and C) modified by compounds containing silver [39] and triclosan [36], *h*—width of suppression zone.

Biotesting of the fabrics and nonwoven materials manufactured by introduction of antimicrobial PET fibers was carried out by the State Center of Surgical Dressing, Sutural and Polymer Materials of the Vishnevsky Institute of Surgery (Moscow). The tests met the requirements of "Methodical instructions on laboratory assessment of antimicrobial activity of the textile materials containing antimicrobial preparations" (Russian Ministry of Health). Twenty-three cultures of bacteria and fungi, including colibacillus *E. coli*, were used during testing.

In the course of heat and wet processing, the fibers lose their ability to suppress vital functions of microorganisms. Stability of antiseptic characteristics of the modified fibers was estimated by subjecting them to repeated processing according to the method described in Ref. [46,47]. The fiber sample was placed into a beaker with a washing solution (5 g of detergent per 1 L of water) heated to $T=45°\text{C}$. The sample was brought into rotation with frequency of 50 ± 5 rpm during 5 min using a magnetic stirrer, then it was rinsed under running water (1 min) and left at room temperature until dry. This processing corresponds to soft conditions (method 7B) of textiles washing in the activator-type machines [48].

Antimicrobial activity of fibers and fabric samples was controlled after each washing.

3.6.3 *Antimicrobial fibers properties*

In the course of crazing modification, PET fibers and products thereof acquire a stable property of suppressing growth of pathogenic microflora on the human body and its environment. In textile technology, PET fibers are used in the mix with cotton, woolen, silk, and other fibers. This allows the regulation of antimicrobial activity of textiles by varying the share of antimicrobial fibers in the mix. At the same time, antimicrobial fibers retain the strength and antifriction properties inherent to PET and make the textile fabrics crease-resistant. The results of assessment of these properties of PET fibers modified by the crazing mechanism and textile materials based on them are shown below.

Experimental samples of PET fibers processed with different antiseptic compounds demonstrate antimicrobial activity, indicators of which are shown in Table 3.4 [49].

Table 3.4 **Antiseptic indicators of the modified PET fibers**

Modifier	Indicator						
	h (mm) after heat and wet processing (cycles)						
	0	**10**	**20**	**30**	**40**	**50**	**60**
Althosan solution concentration (%)							
10	7–9	≤1	0	–	–	–	–
50	8–10	≤1	0	–	–	–	–
Kathamin solution concentration (%)							
10	5–7	≤1	0	–	–	–	–
50	9–10	≤1	0	–	–	–	–
Compound based on triclosan [28]	9–13	8–12	7–11	6–9	4–8	3–6	2–5
Compound based on silver [35]	3–5	3–4	2–4	2–3	1–2	1–2	0

The following conclusions can be drawn based on comparison of these data. Kathamin and Althosan aqueous solutions are intensively removed from the crazes during heat and wet processing of fibers, while the removal rate has little dependence on the solution concentration. Colloidal silver particles trapped in the crazes "work" for long enough. Triclosan is not washed away from the crazes even after 60 fiber processing cycles. It might be considered that the colloidal silver particles and triclosan introduced into PET fibers by the crazing mechanism meet the requirements imposed by the textile industry on the new generation fibers for manufacturing products for personal use and special purposes [50]. Antimicrobial activity of the fibers containing colloidal bimetallic (Cu-Ag) particles is higher than that of fibers containing silver particles, and is comparable with the indicators of activity of fibers modified by triclosan.

The mass of active components of antimicrobial compounds trapped by the crazes is within 0.9%–3.3% of the mass of initial fibers [51].

The pilot batch fibers manufactured by JSC SvetlogorskKhimvolokno are characterized by antimicrobial activity indicators comparable with similar parameters of experimental samples. Range of the initial values of width *h* of the zone of suppression of *S. aureus*, *S. epidermis*, *P.aeruginosa* bacteria growth by bactericidal fibers is 12–15 mm, and by bacteriostatic ones 8–12 mm. Processing characteristics of the fibers pilot batch are presented in Table 3.5.

The data presented in Table 3.5 characterize the change of dimensional and stress-strain parameters of fibers which takes place at their drawing in the modifying compounds: the elementary fiber linear density and diameter decrease, breaking load increases and elongation at rupture decreases. At the same time, it is noticeable that different levels of physical and chemical activity of components of the modifying compounds stipulate the change in draw ratio under approximately identical technological modes of fibers processing on ShA-5K machine.

Table 3.5 PET fibers technological parameters

Indicators and units of measurement	Initial fiber	Antiseptic fibers	
		Bactericidal	**Bacteriostatic**
Actual linear density of an elementary fiber (tex)	0.60	0.49	0.42
Deviation of actual linear density from the nominal one (%)	16.8	−18.3	−29.5
Specific breaking load (mN/tex)	249	332	353
Relative elongation at rupture (%)	172	115	85
Mean diameter of elementary fiber (mcm)	24	21	19

The textile materials containing antimicrobial PET fibers (yarn, fabrics, nonwoven materials) were obtained by the experts at the Center of Scientific Research in the Light Industry (Minsk). The industrial technology to manufacture yarns based on cotton with introduction of antimicrobial PET fibers (linear density of 0.17 tex, cutting length of 35–38 mm) was mastered at cotton-spinning mills Groniteks and Ruchaika. Experimental technologies of obtaining composite yarns for knitting and weaving purposes were developed to determine optimal introduction doses. The plan of experiments was chosen based on the yarn assortment (thickness and purpose) and the need to reduce impact loads of the equipment working elements on antimicrobial fibers. The technological effectiveness and assortment possibilities of the cotton yarns with introduction of 30%–50% of antimicrobial PET fibers have been positively evaluated [52].

Microbiological testing of fabrics with different content of antimicrobial fibers was performed in the accredited laboratory “Scientific Research Institute of Epidemiology and Microbiology” of the Ministry of Health of Belarus. A conclusion on the expressed biological activity of fabrics of optimal composition with respect to *S. aureus* and *E. coli* was received. The antimicrobial effect remains after five dry cleanings of samples. The method of samples contamination (infection) with testing microbes has conclusively demonstrated antibacterial and antifungal activity of fabrics.

Experts of the Central Scientific Research Institute for Complex Automation of Light Industry (JSC TSNIILKA, Moscow) established [53] that the optimal composition of fibrous textile with bioprotective capability is as follows (% by mass): natural and/or chemical fibers—70–95; biologically active fibers—5–30.

3.7 Antimicrobial fibers’ use in medicine and clothing

Textile materials and products that have been engineered to meet particular needs are suitable for any medical and healthcare application in which a combination of strength, flexibility, and sometimes moisture-and air-permeability is required. Materials used include monofilament and multifilament yarns, woven, knitted, and nonwoven fabrics, and composite structures. The applications are many and diverse, ranging from a single-thread suture to the complex composite structures used for bone replacement, and from the simple cleaning wipe to the advanced barrier fabrics used in operating rooms [54].

Over the last few years, the textile industry has developed different methods for obtaining fabrics and fibers with an antimicrobial action for use in hospital environments and for other purposes [55]. With growing public health awareness of the pathogenic effects, malodors, and stain formations caused by microorganisms, there is an increasing need for antibacterial materials in many application areas like medical devices, health care, hygienic application, water purification systems, hospital, dental surgery equipment, textiles, food packaging, and storage [56–58].

Various groups of *antimicrobial substances* belonging to the classes of organic and inorganic compounds are applied with the aim to create biologically active textile materials with wide-spectrum antimicrobial activity and resistance to different processing methods. The most common of them are metals and their salts, salts of quaternary ammonium bases, phenolic compounds, various heterocyclic compounds, including nitrofuran class compounds, antibiotics, antimicrobial dyes, etc.

Silver is the most active antiseptic agent among metals [55]. It is no secret that silver has been used throughout history to combat bacteria. The earliest records show that in ancient days, silver was used to line water vessels during long sea-going voyages. In the middle ages, the Church made its chalices and Eucharist trays of silver to prevent the spread of disease. Although some other metals, such as copper, zinc, and cobalt, have attracted attention as effective antimicrobial agents for textiles, silver is by far the most widely used in general textiles as well as in wound dressings.

For synthetic fibers, silver particles can be incorporated into the polymer before extrusion or before nanofiber formation using electro spinning. The treatment of natural fibers with metals can only be undertaken at the finishing stage and various strategies have been devised to enhance the uptake and durability. Cotton has been pretreated with succinic acid anhydride, which acted as ligand for metal ions to enhance the subsequent adsorption of metallic salts (Ag^+ and Cu^{2+}) and to provide very effective antibacterial activity.

Among these antimicrobial agents, silver has been widely used in many fields because it shows strong biocidal effects on many pathogenic bacteria. In addition, nanosized inorganic particles possess high surface area/volume ratio and display unique physical and chemical properties. Accordingly, the immobilization of silver nanoparticles on various fibers has recently attracted a great deal of attention. Concerning the studies of fiber/silver nanocomposites, most researches have been interest in preparations of ultrafine fiber containing silver nanoparticles. These developments are important and contribute greatly to the textile industry. However, the conventional cotton microfibers are still highly popular in textile markets. Surface modification of cotton microfibers with silver nanoparticles can increase both the price and purpose of the fibers. [59]. For example, today, AgION Technologies, a Nexera-trusted technology partner is using its patented silver based antimicrobial compound to control destructive microbes for use in medical applications, food packaging and more. And now, the same silver based technology incorporated into Nexera's SpectraShield-9900 Series of respirator masks can provide protection from these microbes [60].

The materials impregnated with silver salt solutions (silvered water, silver citrate or lactate, as well as silver chloride) promote wound healing and prevent its suppuration. However, practical application of silver is not feasible, due of its high cost. Besides, direct sunlight causes the decomposition of silver salts resulting in discoloration of the material [61].

Copper compounds have a wide application to impart antimicrobial properties to textile materials due to their low cost, insignificant toxicity, and rather high biological activity. The materials processed with copper salts display a long-lasting antimicrobial effect which remains after repeated washings [62,63].

Along with the metal salts, quaternary ammonium bases (one of which is *Katamin AB*—aqueous solution of alkyldimethylbenzylammonium chloride) are used to obtain biologically active textile materials. Katamin AB is a highly effective antimicrobial disinfectant against bacteria of colibacillus group, staphylococci, salmonella, mold fungi, and yeast. It is recommended for use to treat surgeons' hands, surgical areas and wound surfaces, as well as to disinfect surgical instruments, patient-care items, and rooms [64]. However, Katamin AB displays sufficient antimicrobial properties in concentration not exceeding 1.5% by mass.

The materials containing Katamin AB can be used to produce underwear and bed-linen, special clothing for medical personnel, clothes for work under special conditions, and hospital items. To impart antimicrobial activity to textile fabrics, including nonwoven carriers, a biologically active complex with antimicrobial resistance to pathogenic microflora which consists of Katamin AB in combination with potassium iodide is offered [65,66].

Triclosan (2,4,4-hydrophenyl trichloro (II) ether) is a member of the antiseptic and disinfectant family (see also Section 3.4). Triclosan is a halogen containing derivative of phenol, and is used in cosmetics and toothpastes. It has a wide range of action against gram-negative and gram positive bacteria. This compound, owing to the presence of the acaricide benzyl benzoate, also offers protection against mites and is used in acaricide (spray or powder) formulas, as well as in a solution (25% concentration) for the treatment of scabies. This compound is nontoxic. Benzyl benzoate is an acaricide that acts, chemically, directly on the mites. Due to its antibacterial properties, triclosan has found widespread use in a variety of consumer products including toothpastes, deodorants, soaps, polymers, and fibers [67].

In addition to the aforementioned compounds, phenol derivatives (of which hexachlorophene is of the greatest practical significance) are also used to obtain biologically active textile materials. Hexachlorophene displays high activity against Gram-positive bacteria and possesses fungicidal action. For example, the product of interaction of the cellulose graft copolymer with hexachlorophene has a bond which is rather stable against hydrolysis, therefore textile materials made of this fiber can endure up to 30 washings without noticeable deterioration in their antimicrobial properties. In addition, they reduce microbial contamination of a patient's skin by 3–6 times.

Such fabrics are used to produce underwear and bed-linen for patients staying in hospital after surgery as the result of which their body resistance against the action of microorganisms is weakened [68].

Nitrofuran-class compounds have a wide range of antimicrobial action, high antimicrobial activity, and rather low toxicity. The furagin molecule contains imidohydrogen which is capable to be substituted by metals. In this regard, similar compounds of furagin with certain metals are slightly soluble in water, which allows antimicrobial properties (stable under operating conditions) to be imparted to textile fabrics. Furagin is active against Gram-positive (staphylococci, streptococci) and Gram-negative (colibacillus) microorganisms, with the exception of blue pus bacillus [64].

Antibiotics such as cephalosporin and tetracycline are also used to impart bactericidal properties to textile materials. Clinical studies of antibiotics have shown that the Gram-positive and Gram-negative microflora, including the colon group of bacteria, olms, blue pus bacillus, is sensitive to them [69].

The common carriers of antimicrobial materials are fabrics made of *cellulose fibers* manufactured by simple interlacing with smooth homogeneous surface. Among cellulose fabrics, the fabrics with chemically bonded antimicrobial agents which are characterized by the ability to retain the long-lasting bactericidal effect after repeated washings, sterilizations, autoclave treatment, etc. are of the greatest interest to medicine. For this purpose, cellulose is subjected to preliminary treatment in order to introduce (into the macromolecule) the reactive functional groups capable to interact with bactericidal or fungicidal preparations.

Antimicrobial fabrics made of cellulose fibers are used in production of medical bandages, tissues, sanitary products, underwear and bed-linen, hosiery, and sock liners, as well as protective workwear for persons dealing with dangerous pathogens, plague, anthrax, brucellosis, etc. [56].

Wound dressings intended to accelerate healing of septic wounds and burns, of which application reduces the term of their treatment by half, have been created on the basis of modified cellulose with reactionary active groups of medicinal substances [70].

Tissues made of low-grade *cotton raw materials* with surface density of 120–170 $\mathrm{g\,m^{-1}}$ and content of antimicrobial, antifungal, or deodorizing additive of 10%–70% of the mass of the material are related to sanitary products which are used for domestic and industrial purposes.

Medical bandages representing a sterile cotton gauze or similar textile material with a pharmaceutical carrier in the form of an ointment, paste, aerosol, etc. have found application in treatment of ulcers of the patients confined to bed. For example, a bandage on the base of a plain woven cotton fabric and a layer of medicinal substances reduces microbial contamination of human skin and interrupts the mechanism of infectious diseases transmission [71].

The cotton-fabrics-based hosiery and sock liners have a distinctive mycocide effect resistant to repeated washings. They are applied for treatment and prevention of skin diseases.

Artificial and synthetic fibers and threads are effective carriers of antimicrobial preparations. Therefore, fabrics made of polyvinylalcohol, polyethylenterephthalat, ftorlon, hydrocellulose, and acetate fibers and threads are obtained by introducing various bactericidal agents into a spinning solution or polymer melt. However, they lack the antimicrobial effect resistance to repeated washings. As a result, such fabrics can be used for the products designed for a limited number of washings or intended to be used under conditions where they are not subjected to processing with water. However, as discussed in this chapter, the antimicrobial polyester fibers produced by the crazing technology can endure repeated wet processing with practically no decrease in antimicrobial activity.

Antimicrobial fabrics from polyvinylalcohol, polyacrylonitrile, and polyamide threads are used, for example, to produce sanitary products and hosiery, as well as rugs for hospitals.

Antimicrobial synthetic threads have a wide application in the form of *suture materials—threads*. Such surgical suture represents a new pharmaceutical form of chemotherapeutic preparations to prevent side effects on the human body and tissues which frequently occur when traditional methods of medicines administration are used. According to data from the A.V. Vishnevsky Institute of Surgery (Russia), polypropylene and polycaproamide suture threads possess the highest and prolonged therapeutic action among all known antimicrobial suture materials. Synthetic threads with antimicrobial properties are also used as vascular implants.

In addition to the fabrics, *knitted cloths* have found application as textile carriers for antimicrobial materials. The knitted cloth (unlike the fabrics) possesses good flexibility, elasticity, and stretchability that allows the creation of products in the form of tubes of various diameters and shapes. The type of the knitted material weaving is one of the main characteristics which defines its properties: stretchability, unknitting, shape stability, etc. Knitted cloths with the main types of weaves (jersey structure, rib structure, tricot, etc.) are widely used in medicine.

Knitted fabrics based on polyester and polyamide threads, as well as spindleless spinning cotton yarn with surface density of 140–280 $\mathrm{g\,m^{-1}}$, are used to produce dressing materials [72–74]. They possess high capillary action, lightness, and can be freely separated from the wound surface. High shape stability at washing and resistance to sterilization allow the reuse of products made from knitted synthetic materials (up to 10 times).

Knitted fabrics made of synthetic threads, for example, polyester ones, can be used in bandaging products as an atraumatic layer [75].

Cotton knitted materials with a complex of therapeutic and antimicrobial substances are applied in medical bandages and tissues. They rapidly absorb wound secretions, possess the expressed antimicrobial properties, are characterized by the increased therapeutic effect, provide for dynamic clearing of infected wounds, prolonged medical action, and less frequent change of bandages at practically complete atraumaticity.

For example, AKTIVTEKS antimicrobial bandages and tissues made of cotton knitted fabric are designed for treatment of trophic ulcers and ulcerous defects at diabetic foot infections. They contain medicinal agents of local anesthetic, antiseptic and wound-healing action along with a biocompatible polymer-polysaccharide which swells when moistened and forms a gel, thus ensuring a prolonged introduction of medicines into the wound. Application of AKTIVTEKS tissues increases the efficiency of trophic ulcers treatment because of the fact that, at the first stage, combination of antioxidant and antimicrobial action leads to the improved medical outcomes, while, at the second stage, the combination of antimicrobial and wound-healing action leads to reduction of the healing time [68].

Cotton-lavsan knitted fabrics with antimicrobial properties are used as medical swabs and surgical bandages. They are elastic, can be easily placed on contoured surfaces of wounds and introduced into slit-like wounds (as well as easily and relatively painlessly removed from them); they possess high hygroscopicity and capillarity and ensure drainage (the most important factor of treatment for wound), while their basic properties are as good as the ones of the medical gauze swabs and bandages. The design of products (knitted weaving, plain edge) simplifies operation of cotton-lavsan swabs and excludes the possibility to leave the tiniest threads of dressing material in the wound, which is often the case when gauze swabs are used [76].

Flat knitted mesh cloths made of antimicrobial polypropylene threads have been successfully used in reconstructive surgery for many years, while mesh knitted fabrics made of polypropylene threads in combination with polyamide ones are used (instead of gauze tissues) as antimicrobial dressing for burn wounds [77].

Nonwoven cloths are promising carriers of antimicrobial preparations. Nonwoven fabrics obtained by needle-punching and canvas-sewing techniques, thermal bonding, adhesive bonding, or their combinations are the most widespread ones.

Needle-punched nonwoven fabrics made of polypropylene fibers with surface density of $100\,\mathrm{g\,m^{-2}}$ and higher, as well as the ones based on polyvinylalcohol fibers with chemically bonded antimicrobial agents have found application as biologically active swabs [78]. Since polypropylene fibers have cation- and anion-exchange groups and medicinal agents have basic or acid groups of different ionic strengths, it is possible to control the bonding strength between the two which accordingly provides for the possibility to obtain biologically active nonwoven fabrics with variable time of therapeutic action.

Medical nonwoven material in the form of threadless canvas-sewn cloth made of the bleached modified viscose is used for bandages. It possesses high hygroscopicity, and rapidly absorbs and effectively withdraws the secretions from wounds. Air permeability of a bandage made of such nonwoven cloth is four times higher compared to a cotton gauze bandage.

Thermally bonded nonwoven fabrics made of polyurethane threads are used to produce elastic bandages. Along with high elasticity, they possess good air permeability.

The problem of textile materials "dusting" prevention in surgery has been one of the most important challenges for a long time. Particles of fibers (when they get into an open wound) often lead to granulomas. The use of polypropylene nonwoven materials with latex binders reduces the amount of large (more than $3\,\mu\mathrm{m}$) particles in the wound by 90% compared to cotton fabrics. They are used to produce tissues and sanitary products.

Thus, fabrics, knitted fabrics, and nonwoven cloths are the main textile carriers of antimicrobial materials used in medical practice.

Fabrics and knitted fabrics are used widely enough in *production of clothes, linen*, surgical dressings, sanitary and other products. Nonwoven cloths are not commonly used yet and have come into use mostly as surgical dressings. However, nonwoven antimicrobial fabrics start to be used for production of workwear and bedding items, but most often such products are single-use ones.

Antimicrobial materials used to manufacture *medical wear*, including special clothes for surgeons, occupy an important place. Such clothing not only provides for reduction in postoperative pathologies, but also protects the surgeon against infections, which is particularly relevant with regard to the spread of diseases such as AIDS.

At present, products obtained from woven and knitted textile cloths prevail in the assortment of medical products based on textile antimicrobial materials. Nonwoven cloths are used in production of antimicrobial materials on a limited basis. Antimicrobial materials on nonwoven carriers are used mainly for production of single-use surgical dressings, bandages, tissues, sanitary products, personal hygiene products, medical workwear, and linen (bed-linen, underwear, surgery clothes) [68].

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Fibers of reduced combustibility

4

4.1 Fire-retardants

Fire-retardant agents are flame inhibitors or substances reducing combustibility of materials of organic origin. Mechanism of their action is based on isolation of one of the sources of fire-heat generator, combustible substance, or oxygen. Currently, the production of fire-retardant agents represents a large sector of chemical industry which is evidenced not only by overall indicators of the international market growth, but also by the importance of fire-retarding additives for fire protection. Usually, combinations of various fire-retardant agents creating synergistic effect are used to protect plastic products.

Despite the effect of the global economic downturn, the market for fire-retarding materials continues to grow. Its capacity, according to the survey performed by the Buyer Report, will grow annually by 5.4%; thus, the estimated production output will amount to 2.6 million tons by 2016 [1].

The data on consumption of the main raw materials for fire-retarding compounds are similarly impressive. The demand for flame inhibitors has surpassed the level of 2.2 million tons already by 2014. Moreover, average annual growth rate will fluctuate at the level of 6.9%–7.2%, which will allow an increase of total sales volumes to 7.1 billion dollars by 2017. According to representatives of MarketsandMarkets, the market capacity in 2011 was estimated at 4.8 million dollars. And while the figures for a number of indicators may vary depending on an industry status report, all analysts agree on one thing: the Asia-Pacific Region remains the key player in the market. In 2014, it accounted for about 47.7% of global demand for fire-retardant agents. And the sky is the limit for companies from Taiwan and South Korea, which clearly demonstrate their keen interest in high-quality fire-retarding additives to protect electronics and household appliances. So far, Chinese companies remain the main producers and consumers of fire-retarding agents. According to the data collected by Reportlinker, about 600,000 tons of fire-retarding additives were produced in the People's Republic of China in 2011, and only 200,000 tons had left the country.

The market of raw materials for fire-retarding materials expands at a slightly slower pace in India where tougher requirements on fire safety in commercial and housing construction industry are expected to increase interest in the new generation of flame inhibitors.

Demand for fire-retardant agents in the countries of Western Europe (which were once at the forefront in this area) is increasing at a slightly more moderate pace which itself can be considered as progress for the recession-sodden region. In the United States, on the contrary, the situation looks a little bit brighter. Up to 2016 the capacity of the local market was increasing by 4.6% a year, thus providing for raising the level of sales to 1153 million dollars within 3 years.

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The Russian market of fire-retarding agents amounts to about 90,000 tons. At the same time, several years ago the share of import amounted to more than 70%. Many types of fire-retarding agents are not produced in Russia. High-quality aluminum and magnesium hydroxides are imported; some types of bromine-containing and organophosphorous fire-retardant agents are also imported. Annual growth of consumption volumes is about 10%–20%. The problem of choosing a fire-retardant agent for production of polymer composites is reduced to the solution of the task of optimal combination of "safety-efficiency-cost-compatibility" parameters. Currently, the Russian market for fire-retarding agents is oversaturated by halogen-containing products and is similar to some extent to the aforementioned situation in Asia (China, Taiwan, and South Korea in particular).

The structure of the market for fire-retardant agents is characterized by the broad range of products. The group of fire-retarding agents includes thousands of commercial products containing hundreds of different chemicals which are usually divided into the following main classes: aluminum hydroxide, bromine-containing compounds, organophosphorous fire-retardant agents, antimony oxides, and chlorine-containing compounds. This classification divides fire-retardant agents into groups of products with similar chemical composition and mechanism of action. Most manufacturers specialize in the production of specific groups of fire-retardant agents.

However, while improving fire-resistant properties, fire-retardant agents may worsen other properties of materials. All groups and all individual fire-retardant agents are not without their disadvantages. Therefore, the use of a specific fire-retardant agent depends on its various additional characteristics.

The share of *organophosphorous compounds* is about 14% of the total consumption of fire-retardant agents by volume and about 23% in monetary terms. Consumption of this specific type of fire-retardant agents is growing at the fastest rate, which is explained by both their fire-extinguishing properties and excellent chemical and physical characteristics. Organophosphorous fire-retardant agents can be divided into two groups: halogen-containing (smaller share) and halogen-free. Halogen-containing fire-retardant agents are used mainly in production of polyurethane insulating foams. In addition, they are used in production of coatings and thermoreactive polyurethanes. By combining properties of phosphorus and chlorine-containing compounds, this group of fire-retardant agents possesses magnificent fire resistance.

Halogen-free phosphates are extremely versatile. They are used when a fire-retardant agent should combine low viscosity, solubility, and transparency, should not dye a polymer, and should contain no halogens. These substances are used in almost all types of polymers, except for polyolefins, with which they are incompatible. The majority of halogen-containing fire-retardant agents remain effective. It is widely believed that their substitution with organophosphorous, halogen-free fire-retardant agents reduces the fire protection effect and deteriorates the product properties. However, this statement is incorrect in many instances.

The world market for fire-retardant agents is characterized by toughening environmental standards and an increased share of environmentally safe groups of fire-retardant agents [2]. As a rule, well-known fire-retardant agents are under close scrutiny by ecologists. Moreover, the magnitude of the problem is sometimes related to the possible threat to world safety. This explains the recent UN decision on a total ban of production and use of Hexabromocyclododecane (HBCD) as a fire-retarding additive. The latest researches have confirmed that introduction of these components into the structure of polystyrene foam isolation of buildings can have adverse health effect. In particular, HBCD disturbs thyroid gland functions.

Some large corporations specializing in production of brominated fire-retardant agents have already supported the UN resolution adopted in Geneva. Thus, Albemarle, ICL Industrial Products, Chemtura, and Tosoh are planning to explore the alternatives for HBCD in the near future. Actually, they still have some time as the ban will take effect only in 2019. Until then, all manufacturers will be obliged to label their thermal insulation materials accordingly and render assistance in proper utilization of all out-of-use HBCD-containing products. In addition, it became known that the United Nations had included more than 20 names, including polychlorinated biphenyls and a number of pesticides, into the list of chemical substances subject to mandatory phase-out.

“Prohibitive” practices are widespread in the United States where public safety issues are addressed at the national level. A few years ago the Environmental Protection Agency (EPA) began developing its own inventory of “hazardous chemicals.” At the beginning of 2015 it was submitted for consideration to President Barack Obama's administration. The inventory included polybrominated diphenyl ethers (PBDEs) used as flame inhibitors, as well as some groups of phthalates and bisphenols. According to health care representatives, these substances have negative effects on reproductive function and are the cause of neurological disorders. For this reason, production of some PBDE has already been discontinued forcing, inter alia, ExxonMobil, Dow Chemical, and BASF to commence development of eco-friendly alternatives. In spring 2015, Vermont State authorities supported a ban on the use of chlorine-containing fire-retarding substances. In the 1970s, it was proved that availability of such components in clothes could be the cause of malignant tumors in children. More than 40 years later, the decision was taken to phase out their use completely.

Chlorine-containing fire-retardant agents are widespread in consumer goods. According to recent researches, their increased concentration can be the cause of progression of nervous and reproductive system diseases. Moreover, their level of protection is questionable: many specialists claim that these additives contribute to the spread of toxins during combustion which threatens the safety of fire-fighting services.

Relatively recently, scientists from the American Academy of Pediatrics have established that PBDE, which had been used for decades as fire-retardant agents for furniture, carpets, and electronics, might have an adverse effect on a child’s mental health. The undertaken researches show that PBDE can disturb thyroid gland function; moreover, it may cause hyperactivity in a child and distract, preventing complete assimilation of information.

There have been numerous reports of the danger of PBDE usage as fire retardant additives since they stay in the human body for a long time. Their distribution in the United States was officially forbidden in 2004; it was then associated with health problems of 5-year-old children. Nevertheless, PBDE is still incorporated into various consumer goods manufactured in the country.

It is noteworthy that not only public services representatives, but also consumers' unions and committees for environmental protection, are actively fighting against toxic fire-retardant agents in the United States. In spring 2015, EPA expanded the list of fire-retarding substances subject to mandatory control from 4 to 20 names. Nonflammable chemical compounds used in various products, from upholstered furniture to polyurethane foam and polystyrene foam insulation systems, were among them. According to official information, EPA will assess the toxicity of 12 out of 20 compounds, having divided them into three groups; as of now, several subclasses are defined: brominated phthalates, chlorinated ethers, and cyclic aliphatic bromides. The rest will be defined during the survey process.

European environmentalists try to keep pace with the American colleagues in progressive thinking and efficiency of actions. Voluntary Emission Control Action Programme (VECAP) was established under their initiative and has been successfully implemented for several years. By its nature, it represents the advanced system of business operations and industrial projects organization which is based on the ISO 14001 standard. It enables companies to obtain equal access to information on the latest developments and environmental initiatives.

According to a VECAP report, 2012 showed general reduction of emissions in the manufacturing processes and fire-retarding materials usage in EU countries, which is a great achievement for the organizers of the project. Firstly, implementation of the latest technologies in industrial production enables reduction of tetrabromobisphenol A emissions. In addition, the widespread coverage of the program resulted in a better understanding of consumer preferences; gradually, the content of decabromodiphenyl ethers in the soil and subsoil waters, as well as HBCDs which are part of specialized packaging, has reduced (by 50%). The number of VECAP-certified enterprises has grown to 11. At the moment this list includes not only European industrial sites, but also plants located in the United States and China that are also engaged in fire-retardant agents production.

In response to legislative initiatives and programs to "phase out" fire-retarding additives from the market, research projects are being created to find a commendable alternative to such materials. The NANOFRABS project has been launched in the EU; this aims to create a new type of fire-retardant agents for compounds based on Acrylonitrile-Butadiene-Styrene which possess good fire resistance and are capable of protecting electrical appliances. More effective flame inhibitors will be produced by inclusion of nanofillers increasing both fire resistance of materials and their mechanical stability. In the event of a fire, such substances will contribute to the formation of a thermally and mechanically strengthened intumescent coating on the surface of structures. To achieve the required results, nanofillers will be combined with phosphorus-based fire-retardant agents by dispersion of thin plates and fire-retardant agents in the melted polymer.

Scientists from Austria, France, Germany, the Netherlands, Slovenia, and Great Britain were brought together to work on one of the largest projects in the field of fire protection. The objective of their cooperation was to create a new class of nanostructured fire-retarding composite coatings on biological basis which implementation would be possible in medicine, industrial production, and electronics. The materials that have been produced as a result of long-term experiments consist of the tiniest layers of polysaccharides (carbohydrates with a certain number of sugar molecules bound together) covered with nanoparticles of substances on mineral or biological basis. When applied on a scaffold, the compound performs a number of vital functions: it increases its fire resistance and electrical conductivity, and creates a barrier against microorganisms. The program was also aimed at studying of the so-called surface compounds under which the formulation is strictly limited to the surface of the polymer matrix of the material. The program has succeeded in finding the ways to reconstruct nanostructured composites based on renewable resources.

The sphere of fire-retarding materials has not been overlooked by a concept that is actively promoted by Green Chemistry: the use of biological raw materials. Researchers at the Polytechnic University of Turin (Italy) have presented a new type of fire-retarding compound based on deoxyribonucleic acid from herring milt. It turned out that efficiency of the produced material is comparable to fire-retardant agents which are currently in demand. Scientists have found out that phosphatic groups ensure the formation of phosphoric acid, deoxyribose fragments are the source of carbon, and nitrogenous bases release nitrogen when heated. The fire-retarding additive may respond to an open fire in three ways. Firstly, carbon sources act as thermal insulators by charring and limiting formation of volatile compounds. Secondly, acidiferous material promotes dehydration of cellulose and formation of carbon which is added to the charred products. Finally, nonflammable gas or gases (water vapor, nitrogen, or carbon dioxide) separating the combustible material from oxygen are emitted as the result of the fire retardant agent decomposition.

To verify their assumptions, researchers have checked the reaction-to-fire of the processed cotton specimens using a methane burner. The burner flame was applied to a horizontal specimen for two 3-s applications—no changes had been observed. Ignition was also not observed when a specimen was irradiated with a flow of thermal energy. Nevertheless, prior to implementation of fire-retardant agents based on herring DNA, additional tests are necessary, as it is extremely difficult to carry out quantitative assessment of biopolymer fire-resistant properties by visual affirmation of the fact that cotton flammability is reduced. Although the material is environmentally friendly, production of flame inhibitors from nucleic acids can turn out to be expensive.

The share of main "families" of fire-retardant agents in the world consumption of the product is presented in Table 4.1. In a number of countries, plastics converters do

Table 4.1 **Share of the main types of fire-retardants consumption**

Fire-retardant agents	Share of consumption (%)
Aluminum hydroxide	43
Bromine-containing	21
Organic phosphorus	14
Antimony oxides	8
Chlorine-containing	6
Others	8

not use or limit the use of bromine-containing fire-retardant agents which have an adverse environmental impact, therefore the figures of their consumption are variable [3].

Characteristics of the groups of fire-retardant agents presented in Table 4.1 can be summarized as follows.

Aluminum hydroxide is currently the most consumed fire-retardant agent with an annual growth rate in production of ~3%. This is explained by the low cost of hydroxides, the relative availability of raw materials for their production, but is primarily attributable to the fact that in order to achieve the desirable level of incombustibility it is necessary to introduce (into plastics) larger amounts of hydroxides than of fire-retardant agents of other classes [4].

Bromine-containing fire-retardant agents are widely used as plastic components. Protests by ecological organizations cannot stop it since there is still no cheap alternative to such compounds, which are highly effective in reducing combustibility.

Organic phosphorus compounds suppress (both in its gaseous and condensed phases) the burning of plastics. Due to low smoke formation and lack of corrosion of the equipment at their extrusion processing together with plastics, they meet the modern environmental standards in the most appropriate way.

Antimony oxides slow down the burning of plastic products by forming thin films on them. As synergistic additives to basic fire-retardant agents, they are quite effective, but toxic: the maximum permissible concentration (MPC) in the air of the working zone for $Sb_2O_3$is 1.0 mg/m^3, and for Sb_2O_5 it is 2.0 mg/m^3 [5].

Chlorine-containing fire-retardant agents "operate" in gaseous phase. They are not expensive and light stable, and are introduced into plastics in small concentrations.

Other fire-retardant agents include melamines, organosilicone, inorganic boron-containing compounds, etc.

By the mechanism of interaction with the polymer base, the following groups of fire-retardant agents are distinguished:

- substances which chemically interact with macromolecules;
- foaming or intumescent additives; and
- nonflammable particles which are mechanically mixed with polymer.

Additives of the first group are mainly used to modify thermosets (epoxy, unsaturated polyester, and other resins). These compounds are "embedded" into chemical structure of thermosets without compromising physical and mechanical properties of the product.

Intumescent process results in coke formation and foaming of the surface layer of the burning polymer specimen. Density of the coke layer with cellular structure decreases with an increase in temperature. It protects the material inside the specimen against the heat flow and flame.

Additives of the third group represent powders of chemically inert heat-resistant fillers. They are used to decrease combustibility of all polymer binders—thermoplasts, thermosets, and elastomers.

We shall now discuss the environmental issues that are related to the use of fire-retardant agents in polymer materials. In the event of a fire, dense smoke produced by the combustion products of plastics is the most dangerous factor. Therefore, creation of smokeless plastics at burning of which toxic gases (primarily, halogens harmful to human health and environment) are not released has become a trend in polymer materials science in recent decades. Legislative bodies and consumers of plastic in European countries, the United States, and Japan have joined their efforts to expand the market of halogen-free plastics. The European Commission has forbidden the use of fire-retardant agents which pose a hazard to human health, safety, and the environment. One of the chapters of the EU Directive restricting the use of hazardous substances imposes a ban on the use of bromine-containing fire-retardant agents. According to market research conducted by the consulting company Helmut Kaiser, the world market of halogen-free fire-retardant agents has expanded from USD 1.62 billion in 2005 to USD 2.72 billion in 2010. In China, the demand for halogen-free fire-retardant agents increases annually by approximately 13%. This is the highest rate in the world; the rates in Western European countries and the United States are slightly less (9%–11%).

The tendency to decrease the production of halogen-containing fire-retardant agents encounters natural resistance from the manufacturers of these products. The objective cause for slowdown of the tendency is the fact that fire-retardant agents of that class have high rates of mass-specific efficiency at reasonable cost.

4.2 Fire-retardants for PET fibers modification

Most technical textiles, primarily all non-woven fabrics, are made of natural and chemical fibers. A significant drawback of the latter is their combustibility; thus, their use in textile and other materials results in considerable increase in fire danger. Special laws restricting or prohibiting the use of synthetic materials that can burn in the absence of an open fire are adopted in many countries which clearly show the importance of scientific and practical researches in this area.

In recent years, much attention has been given to the problem of decreasing combustibility of textile materials. This is evidenced by the increase in production of fire-retarding fibers and threads, as well as materials and products on their basis. This is particularly relevant for the increase in fire-resistant properties of synthetic threads for production of technical and non-woven fabrics used for fire hoses, conveyor belts in coal mines and dressing mills, tents, filters, workwear, building materials and structures, sewing materials, and fillers for furniture.

There are three methods of fire-retarding finishing for textile materials, including the ones based on polyester fibers: (1) treatment of the fabric, cloth or finished product surface with fire-retardant agents; (2) physical modification of a fiber (fire-retardant agent introduction by the additive mixing with polymer); and (3) copolymerization of monomers or oligomers with the reaction fire-retardant agent in the process of producing a polymer which is later processed into fibers or threads. The latter method, if it does not result in considerable deterioration of the synthetic fiber physical and mechanical properties, is the most effective one, since, unlike the other two, it provides long-term fire protection of fiber and textile materials irrespective of any processing (washing, dry-cleaning, light and climatic effect, etc.).

The problem of fire protection of fibrous materials is probably most relevant for polyester fibers and threads. Firstly, currently they hold leading positions among all types of chemical and natural fibers, including cotton, by production and consumption volumes. Secondly, they are widely used in pure form or in a mix with other types of artificial (mainly viscose) and natural (cotton, wool) fibers in the areas where fire safety is the most important factor.

At present, only few enterprises in Germany, Japan, and the United States produce (in limited quantities) polyester fibers and threads with permanent effect of fire protection; this is achieved by introduction, in the course of synthesis of poly(ethylene terephthalate) (PET), of multifunctional organophosphorus compounds capable of entering into condensation reactions or ester exchange reactions with PET end groups. Oxa-derivatives of phospholane (methylphospholane, *Hoechst*, Germany) and phosphaphenantren derivatives (*DOP-ITS*, *Zimmer*, Germany; *Phosgard PF-100*, *Zimmer*, Germany; *Ukanol FR 50/1*, *Schill & Seilacher*, Germany) are used as such fire-retardant agents.

The fire protection effect depends on the content (in polyester fiber) of phosphorus introduced with the fire-retardant agent during PET synthesis. Usually, optimal concentration of phosphorus in polymer substrate lies within the range of 0.4%–0.6% by mass, thus assuring the required level of fire-protection properties of polyester fiber which is generally characterized by the oxygen index (OI) value.

The most significant results in creating an industrial technology for producing a polyester fiber of reduced combustibility have been achieved by the German company *Hoechst*, which produced it more than 20 years ago at its plant in Frankfurt am Main under the trademark *Trevira CS* (formerly known under the trademark *Trevira FR*). Currently *Trevira CS* is produced in the form of shiny, dull, and painted fibers (type 270, 3.30–13.0 dtex), textured threads (type 589, 167 dtex), filament yarns (types 691, 692, and 695, 50–300 dtex), technical threads (830–3150 dtex, 192–320 filaments, respectively), as well as monofilament threads (thickness 700–2700 dtex) which production started relatively recently for new areas of application.

In the period from 1995 to 2000, the volume of *Trevira CS* sales to more than 200 enterprises in Europe and other countries increased by 50% (10% increase in 2000 alone). An insignificant number of competitive products is being produced only in Italy, Japan, and Korea. *Trevira CS* is traditionally purchased by EU countries' public sector (90%); however, 10% of the product is already being sold to the private sector. The annual demand for fire-retarding polyester fibers, such as *Trevira CS*, grows on average by 12% and more. For example, in 1997 the production turnover of *Trevira CS* increased by 18% compared to the previous year.

At the International Trade Fair for Home Textiles in Frankfurt am Main in January 2001, *Trevira* GmbH (one of the branches of the broken-up *Hoechst*) presented several new types of polyester fibers and threads of reduced combustibility. In particular, it reported that more than 70 million m^2 of various materials are annually produced on the base of *Trevira CS*, and the production volume totaled to more than 800 million m^2 since 1980.

Physical and mechanical properties of *Trevira CS* fiber (type 270), due to chemical modification of PET by fire-retardant agents, practically do not differ from the standard fiber (type 220), but OI of the former (26%) is much higher than the same index of the fiber without introduced fire-retardant agent (OI equals to 21%–22%). It is known that OI maximum value for *Trevira CS* may reach 29%.

Also of interest is the fire-retardant agent under *Ukanol FR 50/1* trademark, manufacturer—*Schill & Seilacher* (Germany), representing a 65% solution in ethylene glycol (EG) *9,10-dihydro-9-oxa-10-[2,3-di(2-hydroxyethoxy)carbonylpropyl]-10-phosphaphenantren-10-oxide.* Experiments on development of technology for synthesis of PET modified with *Ukanol FR 50/1* were carried out at the pilot projects workshop of JSC Mogilevkhimvolokno (Belarus) [6]. The amount of fire-retardant agent was chosen to ensure that (taking into account its 65% concentration in EG) the content of phosphorus in the modified PET was within 0.3%–0.65% by mass. Thus, the optimal amount of the fire-retardant agent introduced at the initial stage of polycondensation was 11%–12% of the total mass of the melt in the vessel.

The analysis of comparative physical and chemical properties of the commercial and modified PET has shown that the pilot batches of PET granulate produced with the use of *Ukanol FR-50/1* possess the properties which are similar to the known *Schill & Seilacher* specimens. The modified PET fiber has the required level of fire-retarding properties (OI of 27.7% for 0.33 tex fiber and 28.6% for 0.84 tex fiber); in addition, it is characterized by the enhanced ability to dye by disperse dyes and reduced ability for pilling formation.

Nitrogen-containing derivative of phosphonic acid—*T-2 fire-retardant agent* produced by Russian enterprises of low-tonnage chemistry—is the most frequently used substance to reduce combustibility of polyester textile materials. The fabric is processed with this substance in the presence of a cross-linking agent: glycasine. The fabric containing 12%–14% of T-2 fire-retardant agent does not sustain combustion in air (OI of 29%) [7]. The OI is the indicator of polymer materials resistance to combustion, of which a definition is given in Section 4.3.

Processing of PET fibers and blended threads based on PET fibers and cotton with *dichlorotribromphenilphosphate* results in their self-damping-out of fire [8].

Oligomerous or low-molecular polymer *polysulfonildipheniltiophenilphosphonates* (PSF) have proven to be highly effective fire-retardant agents for PET. The fiber modified with PSF with the phosphorus atoms content of 2.5% has an OI of 29%. Melt dropping does not occur when testing the fibers for fire resistance [9].

Ammonium polyphosphate is an effective fire-retardant agent for PET. The introduction of foamed graphite into the mix based on ammonium polyphosphate enhances its fire-retarding action [10].

Fire-retardant textile materials based on unsaturated PET are produced by using the composition which contains pyrophyllite and intumescent additive as a special mix of reagents. Composite material based on PET and 40% *mix (4:2:1:1) of pyrophyllite, ammonium polyphosphate, pentaerythritol, and melamine* has a very high OI of 36.4% [11].

A *mix of fire-retarding compounds* has been developed for PET modification *with the general formula* $R^1\text{-}OC_6X_4RC_6X_4OCH_2CH(OH)CH_2OC_6X_4RC_6X_4OR^2$, where 5–60 mol% have two end epoxy groups at each end of a macromolecule, 15–70 mol%—1 epoxy group at one end of a macromolecule and 5–80 mol% do not contain any epoxy group. In this formula, X is H, Cl, and/or Br, R is $C(CH_3)_2$ or CH_2, R^1 and R^2 are CH_2CHCH_2O and $CH_2CH(OH)CH_2Z$, where Z represents the groups formed at reaction with phenolic, spirit, carboxyl, or amine compounds. Fibers with the increased fire resistance are formed from PET filled with this mix (40%–42%) [12].

Aromatic compounds containing more than 50% of bromine, for example, *ethylene-bis-tetrabromo phthalimide*, are intended to impart fire-retarding properties to polyesters [13].

PET threads, yarn, and textile material on a basis which demonstrates both the reduced combustibility and antimicrobial activity are protected by a patent [14]. Thread- or yarn-composing fibers are formed from the granulate modified by target additives, the first of which contains *phosphorus* or *methyloxyphospholan*, and the second of which has various forms of silver (ions, salts, metal, etc.).

In conclusion, the following should be noted. The formation of crazes makes it possible to introduce the substances which are thermodynamically incompatible with PET (and many fire-retardant agents are such substances) into the structure of fibers. However, specific features of the crazing technology impose a number of limitations on their use. Fire-retardant agent should be in the liquid phase possessing surface activity or should be a part of the surface-active modifying colloidal solution. This is a very tough requirement, which significantly restricts the range of suitable fire-retardant agents.

The trend to phase out environmentally hazardous halogen-containing fire-retardant agents (although they are used in small concentrations) places the developers of fire retardant fibers in a difficult situation. The use of environmentally friendly metal hydroxides as fire-retarding additives implies their introduction into polymer binders in very high concentrations. It can be done by filling, but it is unattainable at crazing.

As noted in Section 2.2, the mass of the target additives introduced into PET fiber by the mechanism of crazing does not exceed 3% of the mass of initial fibers. Such a low concentration of active substance trapped by the crazes shows that not all fire-retardant agents can assure incombustibility of the fibers modified by the method of crazing. Unfortunately, the range of fire-retardant agents which are feasible for using in the crazing technology is quite limited. One way to solve the problem is the development of fire-retarding compositions with synergism-manifested components. Several examples of such compositions are given in this section.

Based on the analysis of the rage of fire-retardant agents with low level of environmental hazard, phosphorus-containing compounds with small amount of synergistic additives can be considered suitable for the use in crazing processing of PET fibers. The effectiveness of such approach is evidenced by the low-combustible PET fiber and the method of its production by the mechanism of crazing which are patented by JSC Vladpolytex (Sudogba, Vladimir district) mentioned in Section 2.3.1 [15]. The fiber is drawn in aqueous adsorption-active liquid which contains cheaper inorganic compounds based on phosphates and ammonium polyphosphates instead of rather expensive water-soluble organic phosphorus-containing fire-retardant agents. When modified by such compositions, cleaning of PET fibers to remove functional additives used at previous stages of processing is not required. The crazing process can be performed in the presence of an oiling agent; as a result, low-combustible PET fibers are produced.

4.3 Estimation of fibers combustibility

The standard in Ref. [16] is the main document which defines the fire and explosion safety of engineering materials, including polymer and composite ones. It regulates properties characterizing the ability of any substance or material (except explosive and radioactive ones) to withstand flame development and propagation. Such an evaluation is necessary to develop fire safety and explosion-protection systems in human and industrial environments.

Solid materials are controlled by 10 parameters: (1) flammability class; (2) ignition, (3) self-ignition, and (4) smoldering temperatures; (5) OI; (6) ability to explode and burn while interacting with water, (7) atmospheric oxygen, and other substances; (8) smoke-developed index; (9) flame propagation index; and (10) toxicity index of the products of combustion. Most of them are applicable to polymer materials. According to the standard, polymer fibers are related to the group of combustible materials which are ignited by an ignition source and can burn independently after its removal. Flammability class of indoor curtains, cloths, bedspreads, etc. determines the fire hazard category of the room and is the basis for choosing the respective technological design standard.

Polymer materials' resistance to combustion is regulated by the standard in Ref. [17]. Specimens in the form of bars are installed horizontally (method A) or vertically (method B) to determine the flame propagation speed (burner is used as the ignition source). The standard does not cover materials that warp and shrink under the influence of fire (i.e., synthetic fibers).

Fire safety of textile materials is determined in accordance with the standard in Ref. [18] which applies to all combustible decorative materials supplied to consumers. A specimen of fabric or nonwoven fabric (size 220 × 170 mm) is fixed vertically and exposed to the flame from a burner. Four parameters are monitored: after-flame time during which the specimen continues to flame after the ignition source has been removed or extinguished; steady-state combustion—the fabric after-flame time which exceeds 5 s; residual smoldering combustion after flame combustion is complete; and run of flame over the surface, i.e., fleece ignition which does not affect the main fabric. According to the results of these tests, the textile materials are subdivided into easily combustible and difficult to combust. Flame propagation indicators depend to a large extent on combustibility of PET fibers which are part of textile specimens.

The method for determination of the OI is specified in the standard in Ref. [19]. The OI is the minimum content of oxygen in a mixture of oxygen and nitrogen, at which candle-like burning of a specimen under specific test conditions is possible. The standard covers polymer materials in the form of films and sheets up to 10.5 mm thick. They are not covered by the standard in Ref. [17] since they warp and shrink under the influence of fire.

The measurement method is as follows. The specimen is ignited and placed into the flow of the oxygen-nitrogen mixture which moves at a speed of 4 ± 1 cm/s. Minimum concentration of oxygen in the mix which sustains combustion of the specimen for a certain period of time (180 ± 3 s) or provides for its burning for the specified length is determined. The first achieved result (out of the two aforementioned ones) is selected

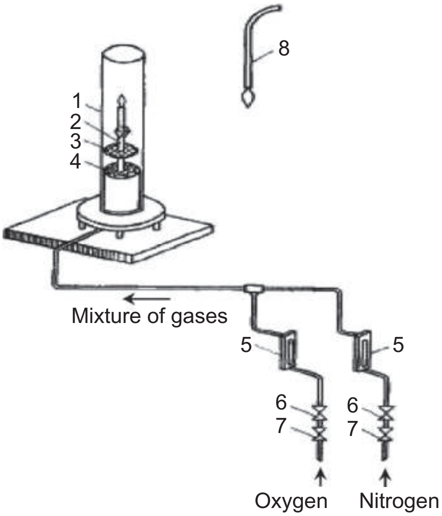

Fig. 4.1 Installation for determining the OI: 1—pipe, 2—specimen holder, 3—mesh, 4—glass balls, 5—rotameter, 6 and 7—valves, 8—burner.

as the criterion for termination of the test. Specimens in the form of standard-sized strips are conditioned at 23 ± 2°C and relative humidity of 50 ± 5% for 88–94 h.

An installation for determining the OI is shown in Fig. 4.1 [19]. Its basic element is a transparent quartz pipe 75 mm in diameter and 450 mm in length, which is placed vertical to the foundation; a gas pipeline is connected to the bottom of the pipe. A layer (80–100 mm) of glass balls 3–5 mm in diameter is spread onto the foundation inside the pipe. The gas mixture flow coming from the pipeline passes through the layer and is evenly distributed across the pipe section. A holder is mounted on the rack fastened to the foundation; it is used to fix the specimen along the pipe axis. A wire mesh for catching particles falling from the burning specimen is installed under the specimen. The gas mixture is delivered to the pipe from pipelines into which oxygen and nitrogen are fed under pressure. Rotameters (instruments to measure gas flow rates) and needle valves for fine and coarse gas flow control are mounted on the pipelines. The specimen is ignited by means of a burner which is entered into the pipe.

The installation is equipped with instruments to measure oxygen concentration in gas mixture (error <1%) and exhaust device for combustion products removal.

The OI (in %) is calculated by the formula

$$\mathrm{OI} = 100V_{\mathrm{o}} / \left(V_{\mathrm{o}} + V_{\mathrm{n}}\right),$$

where V_{o} and V_{n} are volumetric flow rates of oxygen and nitrogen, cm^3/s. The average value of the results of not fewer than three experiments is considered as a final result.

To determine the OI of polymer fibers by this method, it is necessary to make (using these fibers) a rigid specimen which could be installed in the holder in vertical position along the pipe axis. The specimens can be made of the fibers by sintering methods or by extrusion of specimens in the form of rods. In some cases, the researchers of fibers chose to do so, as the result the obtained values of OI are higher as compared to the fiber specimens for 1–2 units. This is due to the fact that, with other conditions being equal, the burning rate of fibers is higher than that of the block specimen. In addition, additional melting which is required for rod formation changes the properties of fibers material distorting the OI values.

The second path which is taken by most of manufacturers and processors of synthetic fibers is the production of specimens by weaving the fibers into braids. This procedure can hardly be standardized due to numerous variable factors: thickness, length and rigidity of fibers, number of fibers in a lock, number of locks in a braid, locks tension when weaving into a braid, weaving step, etc. Any change in these factors will result in changes of free volume of the braid, oxygen access to fibers, and rate of the specimen burning. Therefore, the rules of weaving into braids are usually regulated at the level of the enterprise standard for fibers of one type. Such standards are used by the Research Institute for Physical Chemical Problems of the Belarusian State University and JSC SvetlogorskKhimvolokno. The values of the OI of PET fibers presented in the following section are obtained by specialists of the aforementioned organizations based on the braided specimens.

4.4 Specifics of production and properties of fibers of reduced combustibility

The crazing technology for producing polyester fibers of reduced combustibility was developed in two stages. The objective of the first stage was to assess (using a laboratory bench) the efficiency of fire-retardant agents available in the Belarusian market as the modifiers used under specific conditions of the crazing. The second stage involved the production of the pilot batch of low-combustible fibers which had been used in textiles manufacturing.

Fire-retardant agents’ efficiency as crazing-modifiers was assessed by using (as a parent material) nondirectional PET fibers of brand A (TH 6-13-02047792-88), nominal linear density 0.33 tex (JSC Mogilevkhimvolokno) intended for the nonwoven fabrics production and processing into fabrics.

Fibers were modified using the following fire-retardant agents as active components of process liquids:

- A-1 is the fire-retarding agent based on phosphorus-containing polyesters developed by the Sector of Fire Extinguishing Materials of the Research Institute for Physical Chemical Problems of the Belarusian State University;
- fire-retardant agents manufactured by Bayer (Germany)—type Disflamoll, brands DPK (diphenyl cresyl phosphate), DPO (diphenyl octyl phosphate), TPK (tricresyl phosphate)—used as PET plasticizers;
- ammonium metal phosphates synthesized in the Research Institute for Physical Chemical Problems of the Belarusian State University—brands CuAHS-Ф, CuAHS-ФX, CuAHS-AX, CuAHS-CaX, CuAHS-1, CuAHS-KM;

- ФАХ (FAH) is a universal fire-retardant agent for processing technical fabrics, carpets, wrapping paper, wall-paper which is synthesized in the Belarusian State Technological University;
- F is Firestop PFRA flame retardant manufactured by Firestop Chemical, LTD (England) which is a mix of cyclic di- and triphosphenates; its commercial production has been organized in Volgograd (Russia) at JSC Khimprom under the auspices of JSC Firestop Rus; and
- KA is a complex fire-retardant agent based on aromatic compounds of bromine with antimony oxide and zinc borate additives which is synthesized in Dnepropetrovsk Chemical Technology University.

The following has been taken into account when preparing the modifying compositions and working with them. Fire-retardant agents manufactured by Bayer are toxic substances of different degrees of hazard; it is necessary to use personal protective equipment and follow the strictest safety procedures. TPK shall not be introduced into plastics for household use. SAS and pH stabilizer (10% ammonia solution) were added to the compositions with low F concentration. Synergistic modifying liquid based on F + KA is surface-active without any additives.

Table 4.2 represents composition of modifying liquids containing fire-retardant agents and (in the right column) OI values of PET fibers processed with these liquids in the drawing process. The following conclusions can be made based on analysis of the data presented in Table 4.2.

1. All fibers subjected to processing with the studied compositions are characterized by higher values of the OI as compared to non-modified fibers (OI < 22.5%).
2. An increase in A-1 fire-retardant agent concentration from 10% to 30% (specimens 1–3) results in an increase in OI (24.7% to 27%). It can be expected that at further growth in fire-retardant agent concentration OI will continue to increase. However, an increase of A-1 content in alcohol solution above 30% results in the growth of the modifying liquid viscosity, its irrationally high consumption and ineffectiveness for the process of fibers modification.
3. Modification of fibers with Bayer fire-retardant agents (4–6), even if they are undiluted, provides for OI not exceeding 26.7%.
4. Aqueous solutions of ammonium metal phosphates (7–12) and ФАХ fire-retarding agent (13) are inefficient for PET fibers modification by the mechanism of crazing.
5. Fibers modified by Firestop fire-retardant agent (14) and its mix with KA complex fire-retarding agent (17) display the highest OI values. Dilution of Fairstop with water, even in combination with SAS (15, 16), results in OI decrease as compared to specimen 14.

The Fairstop fire-retardant agent is very convenient for processing the fibers by the method of crazing. This organophosphorous flame inhibitor is effective at introduction into polyester fibers in small concentration typical for crazing technology. It is odorless and stable at temperatures of fibers heat treatment at a staple machine: flash temperature of 146°C, decomposition temperature ~200°C.

The procedure for preparing F + KA suspension composition to modify PET fibers is as follows:

(1) add powdered KA (3% by mass) to liquid Firestop fire-retardant agent;
(2) mix the obtained suspension at temperature of 50°C for 2–6 min.

Table 4.2 **Composition of the modifying liquids and oxygen index of the fibers processed with the liquids**

Composition nos.	Content of components, mass (%)																OI (%)
	A-1	DPK	DPO	TKP	CuAHS-Φ	CuAHS-ΦX	CuAHS-AX	CuAHS-CaX	CuAHS-1	CuAHS-KM	ΦAX	F	SAS	KA	Ethyl alcohol	Distilled water	
1	30	–	–	–	–	–	–	–	–	–	–	–	–	–	35	35	27.0
2	20	–	–	–	–	–	–	–	–	–	–	–	–	–	40	40	25.6
3	10	–	–	–	–	–	–	–	–	–	–	–	–	–	45	45	24.7
4	–	100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	26.7
5	–	–	100	–	–	–	–	–	–	–	–	–	–	–	–	–	24.9
6	–	–	–	100	–	–	–	–	–	–	–	–	–	–	–	–	24.9
7	–	–	–	–	54	–	–	–	–	–	–	–	–	–	–	46	24.5
8	–	–	–	–	–	43.4	–	–	–	–	–	–	–	–	–	56.6	24.4
9	–	–	–	–	–	–	54	–	–	–	–	–	–	–	–	46	24.4
10	–	–	–	–	–	–	–	55.1	–	–	–	–	–	–	–	44.9	24.4
11	–	–	–	–	–	–	–	–	30	–	–	–	–	–	–	70	25.7
12	–	–	–	–	–	–	–	–	–	50	–	–	–	–	–	50	24.9
13	–	–	–	–	–	–	–	–	–	–	100	–	–	–	–	–	24.8
14	–	–	–	–	–	–	–	–	–	–	100	–	–	–	–	50	28.0
15	–	–	–	–	–	–	–	–	–	–	50	1	–	–	–	49	27.2
16	–	–	–	–	–	–	–	–	–	–	40	2	2	–	–	58	26.2
17	–	–	–	–	–	–	–	–	–	–	97	–	–	3	–	–	28.2

The suspension is stable at room temperature for a long time. An increase in concentration of powdered KA above 3% results in its settling out.

A pilot batch of PET fibers of reduced combustibility (100 kg) was manufactured at JSC SvetlogorskKhimvolokno.

In preparation for manufacture, it turned out that production of Firestop fire-retardant agent in Russia had been stopped since the end of 2009. The decision was taken to replace Firestop with liquid Pekoflam NPP fire-retardant agent manufactured by Clariant CmbH firm (Germany). It is an inorganic halogen-free phosphorous compound. It has the following characteristics: density 1.24 g/cm^3, viscosity 0.05 Pa s, setting and boiling points 0 and 100°C. Such characteristics allow the use of Pekoflam for modification of fibers at processing on a staple unit, but they are indicative of the necessity to decrease temperature below 100°C in a drying chamber for staples—milled fibers. Though Pekoflam is classified as non-hazardous material, the company recommends observing all precautionary measures during its handling to prevent contact with skin, eyes, and respiratory tract.

Experiments on processing the fibers at a laboratory bench have shown that Pekoflam efficiency is quite high; however, it is lower than the one of Firestop fire-retardant agent. Pekoflam dilution with ethyl alcohol reduces its modifying effect. This means that its efficiency as an inhibitor of fibers burning is limited by this specific property and not by activity of the fire-retardant agent as the microcrazing initiator.

The fibers were processed at the rate of 22 m/min with the drawing ratio in the area of modification of 2.5. An ammonia smell occurred as the bundle passed through the corrugating unit. In spite of the fact that measurements of air in the working zone made by public health services showed that MPC did not exceed the norm, temperature in the drying camera for staples was decreased to 98°C.

PET fibers of the pilot batch had OI = 26–27; their physical and mechanical parameters are presented in Table 4.3.

Work on producing PET fibers of reduced combustibility has led to the following conclusions. The crazing technology makes it possible to introduce (into the structure of a fiber) a modifier in the amount not exceeding 3% by mass; the technology can be successfully implemented only when using the most effective fire-retardant agents which nomenclature is quite limited. Most fire-retardant agents reduce combustibility

Table 4.3 **Physical and mechanical characteristics of PET fibers of reduced combustibility modified with Pekoflam fire-retardant agent by the crazing technology**

Parameter description (unit)	**Parameter values for fibers**	
	Initial	**Modified**
Actual linear density of an elementary fiber (tex)	0.60	0.49
Deviation of actual linear density from the nominal one (%)	16.8	−17.2
Breaking tenacity (mN/tex)	249	290
Relative elongation at rupture (%)	172	127
Diameter of elementary fiber (mcm)	24	21

of fibers to acceptable level by filling a polymer binder in concentrations which are by an order of magnitude higher. This natural limitation is the main factor which determines the area of the crazing technology application for producing synthetic fibers of reduced combustibility.

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Aromatized and repellent fibers

5

Aromatic agents (from the Greek *árōma*, frankincense) are fragrances of organic nature with pleasant odor. The majority of aromatic compounds contain benzene rings—benzene and its bi-, tri-, and polycyclic compounds. Currently, much attention has been given to aromatization of textile materials in order to increase consumer demand. About 70%–80% of buyers make a judgment on a product's properties (such as freshness, sophistication, originality) based on its odor. It has been statistically established that the sales volume increases in the shops where the air is saturated with the vapors of aromatic agents. Textile products are impregnated with solutions of aromatic agents; aromatic compounds are introduced into the fibers, yarn, and threads during technological processing. The technology of crazing attracts with the possibility to introduce any aromatic agent into the fibers and probability of their prolonged release from the crazes.

5.1 Aromatic agents for textile materials

At the beginning of the 20th century it was suggested that trees and grass discharge special substances (atmovitamins) which are digested by lungs and are catalysts for biochemical processes in the human body. Air ions, ozone, as well as essential oils (volatile liquids of complex chemical composition produced by plants) are related to atmovitamins. Each essential oil contains more than 150 volatile compounds, the smell of which affects the organism in different ways. This fact explains the variety of pharmaceutical and therapeutic properties of essential oils [1–3].

Organic compounds which are a part of essential oils are divided into eight major classes [4].

1. Aldehydes have antiinflammatory, calming and antiviral effects on organism. Essential oils high in aldehydes have a characteristic lemon-like smell. These are lemongrass, lemon balm, citronella grass, and lemon eucalyptus oils.
2. Ketones are a class of chemical compounds which possess wound-healing properties and ease the secretion of mucus from tissues. The ketones' unique ability to stimulate cell growth has been utilized in cosmetology. Camphor oil is almost pure ketone. Other essential oils with high ketone content include rosemary, sage, eucalyptus globulus, and hyssop.
3. Alcohols have bactericidal, antiviral, vitalizing, and diuretic effects. The pancreas produces 32 kinds of alcohol for use in human metabolism. Linalool and terpineol essential oils which possess bactericidal properties belong to this group. Essential oils of rose, bitter orange, peppermint, myrtle, tea tree, sandalwood, patchouli, and ginger are rich in alcohols.
4. Phenols are compounds with a very strong bactericidal effect; they have immunostimulating, invigorating, and warming effects; however, they can irritate the skin and produce slight liver toxicity if taken in high doses for extended periods of time. In the pharmaceutical industry,

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phenols are used in hygienic lipsticks and cough drops. Clove, cinnamon, thyme, marjoram, savory, and cumin essential oils are rich in phenols.

5. Terpenes are natural hydrocarbons with general formula of $(C_5H_8)_n$ which have antiviral properties and are potential skin irritants. Pine oil is used to produce terebenthene (turpentine). Oils with a high amount of terpenes include lemon, orange, bergamot, black pepper, pine (wood and needles), nutmeg, and angelica. Terpene molecules are the smallest in comparison with the size of molecules of other compounds contained in essential oils. They are quick to get into the respiratory tract and also quick to evaporate.
6. Sesquiterpenes $(C_5H_8)_3$ are a group of terpenes consisting of long carbon chains. The essential oils with high content of these compounds are viscous and long-lasting in their smell. More than 2000 sesquiterpenes have been isolated from roots of wood and green parts of plants. They are contained in essential oils of blue chamomile, immortelle, tansy, yarrow and marigold. Sesquiterpenes possess antiinflammatory, calming and antiviral properties and have bacteriostatic and immunostimulating effect.
7. Esters are products of reaction between alcohols and acids and are the most neutral of the essential oil components. They possess antifungal, calming, spasmolytic, fungicidal and antiinflammatory properties and have harmonizing effect upon the organism. Chamomile, lavender, clary sage, bitter orange, and bergamot essential oils are characterized by a high content of esters. Lactones are cyclic esters of carboxylic acids used as aromatic and medicinal substances. They are some of the strongest antiinflammatory compounds. Arnica essential oil, which is more effective (than ketones) in discharge of mucus from living tissues, is rich in lactones.
8. Ethers (phenylpropane esters) are very harmonizing to the nervous system. They are antiseptic, stimulant, expectorant, spasmolytic, and diuretic. Cinnamon, clove, anise, basil, tarragon, parsley, and sassafras oils have high content of ethers. They are characterized by a "sweet" smell.

Two groups of aromatic agents deserve special mention: odorants and lavender essential oil.

Lavender essential oil (lavender is a species of herbs and shrubs of mint family), according to marketing specialists, is experiencing an "upswing" in demand in the cosmetology, household chemicals, and textile industries [5,6]. The attractive scent of lavender promotes calm and relaxation. Lavender is useful for treatment of hyperexcitability, insomnia, and stress. Lavender oil has a positive effect on human respiratory tract and possesses antiseptic, antimicrobial, and antiviral properties; it is therefore used for treatment of bronchitis and bronchial asthma. Lavender is used for treatment of skin diseases (eczemas), primarily of neurogenic origin, as well as septic wounds and burns [7–9].

The use of lavender oil as an air fragrance in shopping centers results in the increase in sales owing to the effect upon the psycho-emotional state of the buyers. By aromatizing the air in production premises, some Japanese companies have achieved an increase in labor productivity and quality of the operations performed and a considerable reduction of viral diseases.

Odorants are synthetic and natural fragrances intended to impart long-lasting odor to industrial products and capable (if necessary) "to suppress" the smell of the product base material [5].

Essential oils have dominated as odorants for a long time, but the development of the chemical industry led to expansion of the range of their synthetic analogs. Natural components of odorants are mixes of natural biologically active substances. The technological process of their extraction from natural raw materials has a strong impact on their price. When essential oils are used as the base for odorants, it is necessary to adjust carefully the doses of synthetic substances to be added to the base. The disadvantage of essential oils as components of odorants is that they are quick to evaporate and may produce an absolutely unexpected smell in combination with synthetic aromatic agents. Therefore, the use of synthetic odorants that are not burdened with the ballast of unnecessary substances is preferable in many cases. An important technological task being solved using the synthetic odorants is to slow down the release of volatile substances and, consequently, to increase the odorant lifetime.

France, Germany, Belgium, England, and the United States are the main countries for odorants production. Chemical composition of a specifically "sounding" odorant is, as a rule, the manufacturer's intellectual property; therefore, it is very difficult to reproduce the odorant's formulation and unique aroma. The odorants used in the textile industry undergo multistage testing for safety [10]. In particular, a special toxicological assessment is required to determine the so-called skin resorptive effect, i.e., the ability of preparations to infiltrate through the undamaged skin's barrier and have a negative effect for the organism. Another test is the assessment of the odorant's irritant effect, i.e., skin reaction to application of the product (edema, erythema, etc.). Odorants have a clear-cut dependency which is called the "dose-response relationship" in toxicology. In other words, higher concentrations of odorants may cause greater problems.

Synthetic odorants provide for the possibility of unlimited synthesis of scents: from flower, fruit, "edible" to emotional ones, such as "sea breeze," "freshness," or "sweet woman." Concentration of components exerts a significant influence on the shades of an odorant's smell. The compatibility of the odorant's basic components is very important.

The costs of the odorant's production are determined by inclusion of expensive ingredients—natural essential oils or chemical compounds of "special" group which price may be up to several thousand dollars per kilogram. The most expensive aroma compositions are used in the production of perfumes and eau de toilettes; the cheapest ones are used in the production of household chemical goods. The price of odorants may vary from 4 to 150 €/kg. The share of odorants in the product mass is 0.15%–1% in cosmetic products and 5%–20% in air fresheners.

5.2 Modifying compounds with the smell of lavender

5.2.1 Initial substances

Two types of aromatic agents have been chosen for fibers modification by the method of crazing: a natural one—lavender essential oil (*Lavandula latifolia*, manufacturer JSC Botanica, Russia); and a synthetic one—odorant "1-74469 GB Rosemary and Lavender" (Belmay Ltd, England). Distilled water, ethyl alcohol, and three SAS grades—Genapol PF40, Hostaphat KL340D, Emulsogen HSW049 (all manufactured by Clariant Int. Ltd, Germany)—were used in compositions. Solid antiperspirant "Gillette" (manufacturer "Gillette Co.," Boston, USA) was used as a standard for assessment of the odorants' evaporation rate.

Lavender essential oil (designation EO, Russian State Hygienic Registration Certificate No. 08-33-2.81571) is produced by hydrodistillation from the blooming part of medicinal lavender and represents a colorless or yellowish-greenish liquid with light, delicate, cold aroma of lavender flowers. Chemical composition: cineoles (ketone); caryophyllene (sesquiterpene); aeronil acetate, lavandulyl acetate, linalyl acetate (esters); borneol, geraniol, lavandulol, linalool (alcohols); and limonene, pinene (terpenes).

"1-74469 GB Rosemary and Lavender" odorant (O) is 3,7-dimethyl-1,6-octadienetriol. This transparent oily liquid is classified as a skin irritant preparation according to Directive 1999/45/EC.

Genapol PF40 (G) is colorless or slightly cloudy liquid. It is a low-foam SAS with high dispersing ability which is used (in the amount of 1%–3%) in washing and cleaning agents.

Hostaphat KL340D (H) is colorless or slightly cloudy liquid. It is an effective oil-in-water emulsifier. High value of hydrophilic-lipophilic balance allows the production of stable emulsions with oils of different polarities. Its concentration (as the main emulsifier) in water is 1%–3%.

Emulsogen HSW049 (Em) is colorless or slightly cloudy liquid. It is an effective means for obtaining EO emulsions and aromatic agents in aqueous-alcoholic and aqueous compositions. Recommended ratios are: 1–2 g per 1 g of EO or aromatic agent.

Formulations of modifying compositions with natural EO which possesses reflex activity and contains synthetic odorant exerting an associative effect on the human psycho-emotional sphere have been determined as follows.

Based on recommendations [11] and technical characteristics of the selected odorants, the range of the component concentrations in the modifying compositions was determined: aromatic substances 1%–5%; SAS 1%–5%; alcohol 30%–50%; the rest is water. Modifier compositions being analyzed are presented in Table 5.1.

Table 5.1 **Formulations of aromatizing compositions**

Composition no.	Components and their content (% by mass) in compositions						
	EO	**O**	**G**	**H**	**Em**	**Alcohol**	**H_2O**
1	1	–	–	–	–	34	65
2	1	–	3[a]	–	–	–	96
3	1	–	–	3[a]	–	–	96
4	1	–	–	–	3	–	96
5	2	–	–	–	–	33	65
6	3	–	–	–	–	32	65
7	5	–	–	–	–	55	40
8	5	–	–	–	7	55	33
9	–	3	–	–	–	32	65
10	–	3	–	–	3	–	94
11	–	3	–	–	5	32	60

[a] To obtain a homogeneous solution, "water-SAS" mix was heated to $T=40$–50°C.

5.2.2 Compositions preparation procedure

To obtain compositions 1, 5, 6, 7, and 9, EO or O was dissolved in alcohol. Adding water to the solution resulted in the formation of emulsion. Emulsions 1, 5, and 6 started to break in 10–15 min. Emulsions 7 and 9 remained stable for 1–1.5 h and (after disintegration) they became homogeneous again at slight jarring.

SAS-containing compositions 2–4, 5, and 10 were prepared as follows: (1) SAS and water were mixed (G and H, when being mixed, require heating to $T = 40–50°C$); and (2) EO or O was added to the mix. Such compositions are more viscous compared to the alcohol ones and, therefore, are more stable; disintegration starts in just 40 min.

Compositions containing SAS and alcohol (8, 11) are prepared as follows: (1) Em is mixed with water (the mix is transparent and slightly viscous); (2) EO or O are introduced into the mix (which becomes cloudy); and (3) alcohol is added, then composition 8 becomes absolutely transparent and stable and composition 11 remains cloudy.

A group of five experts was established to perform an organoleptic evaluation of compositions. A drop of the composition being analyzed was placed on strips of filter paper. Each expert performed an independent evaluation of the aromatized strips smell with respect to its intensity and stability in time using a three-point scale. The evaluation was performed again in 1, 3, and 24 h. Overall results of the analysis are presented in Table 5.2.

It was concluded that compounds 7, 8, 9, and 11 had the most intensive and long-lasting smell. However, compound 8 was technologically complex in preparation and had the highest costs, while emulsion 9 was less stable in time compared to compound 11.

Table 5.2 **Results of organoleptic evaluation of aromatizing compounds**

Composition no.	Evaluation of the scent intensity by experts (I–V) (score)				
	I	II	III	IV	V
1	1	1	1	1	1
2	1	1	1	1	1
3	1	1	1	1	1
4	1	1	1	1	1
5	2	3	2	2	2
6	2	2	3	2	3
7	3	3	3	3	3
8	3	3	3	3	3
9	3	3	3	3	3
10	3	3	2	3	2
11	3	3	3	3	3

Notes: 1—slight scent of lavender; 2—expressed scent of lavender; 3—intensive, long-lasting scent of lavender.

5.3 Manufacturing and testing of aromatized fibers

Two process liquids have been used for production of aromatized fibers, one of which (compound 7) contained lavender essential oil as an active agent, while another one (compound 11) contained a synthetic odorant with smell of lavender.

The fibers were modified using a test bench described in Section 2.4 (Fig. 2.14). Temperature of the process liquid in a tray was 20–25°C, fibers travel speed 4–5 m/min, draw ratio 2.1–2.5, the fiber drawing point located in the liquid. After the fiber had left the tray it was subjected to thermostabilization by passing through a tube-type furnace at a temperature of 90°C.

The smell stability and amount of aromatic agent in fibers was evaluated by organoleptic and weight methods.

5.3.1 *Weight method*

In between the control weighings, the weighed portions of the newly prepared fibers (mass of 1 g) were stored in air-tight bags at room temperature. The results of assessment of the aromatic agents' evaporation in the initial state and from the fibers modified by the mechanism of crazing are presented in Fig. 5.1.

The following conclusions can be drawn based on analysis of these data. The main challenge in aromatized fibers creation is to ensure the prolonged evaporation of active component of aromatic agents. From Fig. 5.1A it is obvious that evaporation of lavender oil (curve 1) occurs in two stages: the most active EO components with strong smell evaporate in the first 10–20 min (according to experts), then the evaporation rate slows down and remains constant until the smell has completely disappeared. Feasibility of the use of synthetic aromatic agents (curve 2) which evaporation rate is considerably lower compared to the natural ones becomes clear. The efforts of perfumery products creators are focused on the conversion of odorants into the gel form in which the rate of active components evaporation decreases by an order of magnitude (curve 3).

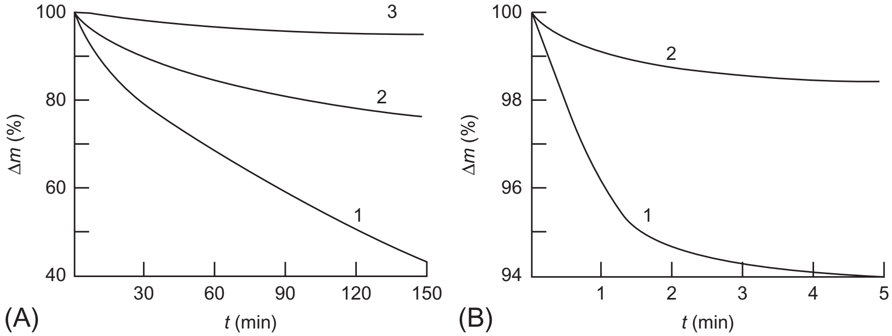

Fig. 5.1 The kinetic of weight loss by aromatic agents in the as-delivered state (A) and aromatized fibers (B). Aromatic agents: 1—EO, 2—O; 3—"Gillette."

These conclusions are confirmed by a graph presented in Fig. 5.1B. It can be seen that:

- **(i)** the rate of evaporation from the fibers of synthetic odorant (curve 2) is considerably lower compared to the natural one (curve 1);
- **(ii)** EO evaporation from the fibers (1) occurs in two stages: in the first 1–2 days the rate is high, but then the rate decreases to a low value and remains almost constant until the aromatic agent trapped in the crazes has completely evaporated; and
- **(iii)** the flat part of curve 1 corresponds to EO evaporation which is constrained, apparently, by the surface phenomena of essential oils bonding with the walls of nano- and microcracks in the fiber which are newly developed in the process of crazing.

The shape of curve 1 in Fig. 5.1B gives grounds to assert that evaporation of volatile modifiers trapped in the crazes has a prolonged duration. It confirms the hypothesis on steric restrictions on discharge from the fibers of modifiers located in the crazes, and consequently the feasibility of improving the technology for obtaining odorized polyethylene terephthalate (PET) fibers. Comparison of the graphs in Fig. 5.1A suggests that creation of conditions for phase transformation of the modifying liquid in the crazes would be a very promising direction. Transition of the liquid located in the crazes into less volatile solid or gel state has to occur at subsequent technological processing of the fibers.

5.3.2 *Organoleptic method*

The following initial aromatic agents have been used as a standard for smell: lavender essential oil and odorant "1-74469 GB Rosemary and Lavender."

No fewer than five specimens of 1 g mass were cut from each bundle of fibers. The fibers specimens were placed into vessels (capacity 200 cm^3, height 100 cm), the standards for smell (in the amount of 0.01 g) were separately placed into similar vessels, then the vessels were hermetically closed. After 1, 3, 24, and 48 h, five experts performed organoleptic evaluation of the aromatization effect of the fibers and compliance with the smell of the standard using the five-point scale. The results of the analysis are presented in Table 5.3.

Table 5.3 **Aromatization effect of experimental specimens of PET fibers**

	Aromatization effect of specimens (score[a])			
	Lavender essential oil		Odorant	
Holding time (h)	Standard	Fiber	Standard	Fiber
1	5	4	5	4
3	5	3	5	4
24	4	3	5	4
48	4	2	5	3

[a] 1—has no lavender smell; 2—slight smell of lavender; 3—expressed smell of lavender in 3 min after opening the vessel; 4—expressed smell of lavender during 5 min after opening the vessel; 5—stable expressed smell of lavender.

Table 5.4 **Change of mass of the aromatized fibers (compound 1) depending on drying conditions**

	Loss of weight (%)		
Drying conditions	**Immediately after drying**	**In 12 h**	**In 24 h**
$T = 130$°C, during 30 min	8.0	+3.0	6.7
$T = 60$°C, during 30 min	1.5	2.1	2.4

The table data confirm the availability of the aromatization effect and compliance of the fibers' smell to the standards used as aromatic agents in the modifying liquids. The aroma of the fibers modified by a liquid based on the lavender essential oil weakens more intensively compared to the odorant-modified fibers.

A loss of mass of the aromatized fibers during drying and storage was evaluated using the specimens in the form of bundle of fibers 500 mm long. Results of experiments with the EO-modified fibers are presented in Table 5.4. Based on the analysis of the data, the following conclusions can be drawn:

- increase in mass of the specimens which had been dried at 130°C in 12 h after drying is indicative of two concurrent processes: fibers are losing the aromatic agent which is being evaporated and the dehydrated fibers are adsorbing water contained in ambient air;
- the drying mode at 60°C is more gentle, therefore, after 24 h the fibers still have the introduced aromatic agent; and
- in the first approximation, we can assume that in the process of drying at 60°C the loss of the aromatic agent is from 1/4 to 1/3 of the amount introduced into the fiber.

The expert evaluation has shown that drying at 130°C results in almost complete loss of the lavender smell by the specimens. Therefore, drying conditions for the fibers aromatized by the mechanism of crazing need to be optimized according to the smell preservation criterion.

Thus, evaporation of the natural lavender oil introduced into the fibers by the mechanism of crazing occurs in two stages: with a high rate in the first 1–2 days and with a low, almost constant rate until the aromatic agent trapped in the crazes has evaporated completely. Apparently, the second stage of evaporation corresponds to the oil discharge phase which is physically and chemically bonded with the walls of nano- and microcracks in the fiber which are newly developed in the process of crazing.

5.4 Repellent fibers, their range and application

The protection of humans and animals against blood-sucking insects is a topical issue, the solution of which involves textiles in an important role. Chemical preparations (insecticides) are used to fight against insects. The textiles containing insecticides are used not only to prevent insect stings, but also to prevent transmission of infectious diseases which are spread by blood-sucking carriers from a sick person or animal to a healthy one (encephalitis, leishmaniasis, malaria, etc.). For this purpose the textile fabrics are impregnated with repellents—chemical preparations which discourage insects from landing on skin and other surfaces. The main deficiency of the method is short duration of protection and high consumption of preparations.

The introduction of repellents by the mechanism of crazing into polyester fibers which are presently a component of practically all textile fabrics may be an alternative solution. The choice of repellents as an active component of fibers is determined by the mandatory requirement that the modified fibers should be safe for humans. The textiles may come in contact with skin, exerting influence on its damaged areas and mucous membranes. In this respect, the discouraging preparations are less hazardous than the insecticides which kill insects. Unfortunately, the majority of repellents belong to the group of easily volatile substances which evaporation considerably reduces the period of the fibers' active effect. Solution of the problem of increasing the protection period is topical for the repellent fibers crazing technology.

5.4.1 Range of repellents

The world assortment of repellents includes about 250 active substances [12] which are known under their short conventional names assigned by the International Standardization Organization (ISO). Companies produce tens of thousands of commercial preparations under other proprietary names, giving rise to a multitude of synonyms. The repellents range is constantly updated. It is associated with the appearance (in the insects class) of races resistant (tolerant) to repellents, as well as with aspiration to create repellents which are more effective and safe for people and the environment.

Chemical groups of repellents include the substances having identical chemical structure of active component.

Natural compounds and their synthetic analogs are the largest group of repellents. *Pyrethrins* are substances contained in flowers of pyrethrum and their more effective and stable synthetic analogs (pyrethroids), which form one of the most important groups of repellents, are of the greatest practical value (permethrin, cypermethrin, deltametrin, tetrametrin).

The group of natural repellents includes essential oils of cinnamon, rosemary, cedar, peppermint, etc. For example, "RAPTOR" (Hidalgo Company, Russia), a typical representative of such repellents, consists of a mix of clove and fir oils. Their action is weak and short lived.

Organochlorine compounds are represented by the preparation under the name DDT (dichloro-diphenyl-trichloromethylmethane) with a broad action spectrum. In 1948 the Nobel Prize was awarded to Swiss chemist Paul Müller for his discovery of DDT's insecticidal properties. DDT was banned from use in agriculture in many countries due to its ability to accumulate in fatty tissues of humans and animals and high resistance to biodegradation in the environment.

Synthetic analogs of DDT that do not exhibit its negative properties are used to fight against flies, mosquitoes, and clothes moths. Despite the trend to reduce production of organochlorine preparations, their consumption is still rather high [12].

Organophosphorous compounds are one of the most important groups of modern insect repellents. They are characterized by high activity at moderate consumption rates, broad action spectrum against vermin and rather quick decomposition in environment with formation of nontoxic products. They are ethers, thioethers, ether amides of phosphoric, and phosphonic acids with a general formula of RR′P(X)Y. There are 70–80 organophosphorous preparations in the global assortment of repellents. The following are the most effective ones:

- *thiophosphates* are very effective against blood-sucking insects and mites, but they are toxic to humans;
- *dithiophosphates* are used to fight against household insects; these substances are moderately persistent (they decay in 10–15 days);
- *phosphates*, which typical representative is dichlorvos, $(CH_3O)_2P(O)OCHCCl_2$, provide an effective means against moths, khapra beetles, and other household insects; *amidophosphates* are activated in the insect organisms by releasing acetyl groups; and
- *phosphonates* is a small group of organophosphorous compounds, the most important one of which is *trichlorfon* or *chlorophos* used to fight against household insects and after prohibition of DDT—in large quantities—against dipterous and lepidopterous insects.

Carbamates are represented by a group of compounds, very few of which have found practical application.

DETA (diethyl toluamide), $CH_3C_6H_4CON(C_2H_5)_2$, and less active *dimethyl phtalate* (DMP) are studied well, tested numerous times and recommended by WHO as repellents. DMP is used as a DETA solvent which has synergistic effect. Over the last 50 years, biological activity of more than 3000 carbamates have been determined. The activity of about 30 of them was higher compared to DETA standard; thus they were classified into the highest and first categories of efficiency.

There is a threshold concentration of repellent vapors below which the effect of the latter upon olfactory sensilla (sensitive formations which function as organs of touch, taste and smell in invertebrates) is not seen. According to the value of threshold concentration, repellents form the following sequence: DMP > DETA > pyrethroids. Therefore, combination of repellents creating synergistic effect is the most effective method to repel insects. The range of repellents available in the market of CIS countries is presented in Table 5.5.

According to Euromonitor Int. data, in 2010 the insecticides market volume in Russia amounted to 4150 billion rubles. The share of repellents amounted to one-fifth of the volume of sales, while the share of insects-killing insecticides was fourth-fifths. The large capacity of the market for insecticides is, to a large extent, related to the fact that the duration of the period of fighting against insects of all kinds is not limited, while the season of blood-sucking insects discouraging by repellents lasts for only 2–3 months. Insignificant fluctuations of the market capacity are related to weather conditions and the amount of insects. According to Euromonitor Int.

Table 5.5 Repellent brand names and manufacturers

Trade name	**Manufacturer**	***Active agent*; kind of insects**	**Product form**
“Alphacide”	“Raptor,” Russia	*Azomethiphos*; house flies	Water soluble pellets
“Alfacron”	“Combat,” England		
“Detaftol”	“Raptor,” Russia	*DETA*; mosquitoes, black flies, biting midges	Aerosol spray bottles
“Difox”	“SC Jonson,” Russia	*Dichlorvos*; flies, mosquitoes	
“Dichlorvos”	“Chemist,” Russia		
“Karbozol”		*Karbofos* + *Dichlorvos*; flies	
“Neofos”	“Fumitox,” Russia	*Neopynamin* + *Dichlorvos*; flies, mosquitoes	
“Nefrafos”		*Dichlorvos*; flies, mosquitoes	
“Oksaftal”		*DMP* + *oxamat*; blood-sucking flies	Emulsion
“Perry-l”	“Mosquitall,” Italy	*Permethrin* + *Dichlorvos*; flies, gnats, mosquitoes	Aerosol spray bottles
“Perfos-L”			
“Pesquard NS”	“Upeco,” Spain	*Permethrin*; flies	
“Peritrol-L”	“Veda,” Russia	*Pyrethroids*; flies, mosquitoes	Aerosol spray bottles
“Pif-Paf”	“SC Jonson,” Russia	*Permethrin*; flies, mosquitoes	
“Safrotin”	“SC Jonson,” Russia	*Dichlorvos*; flies, mosquitoes	Aerosol spray bottles
“Fenzol-L”	“Fumitox,” Russia	*Permethrin*; flies, mosquitoes	
“Fenaks-2”		*Boric acid*; flies and their maggots	Powder
“Komarex”	“Gardex,” England	*Dichlorvos*; flies, mosquitoes	Aerosol spray bottles to protect children
“Antikleshch”	“Hidalgo,” Russia	*DETA*, mites	Aerosol spray bottles
“Tri-Tec 14”	“Raid,” USA	*Cypermethrin* + *Pyrethrins*; blood-sucking flies, gadflies, mites	
“Gardex”	“TOSVAR,” Italy	*DETA, propellant, odorant*; mosquitoes	

predictions, the Russian market of repellents will grow 15%–20% annually in the next 3–4 years and the products against flying insects will take half of the market in monetary terms.

In recent years consumers have paid attention to both efficiency and safety of preparations containing special repellents which may be used by highly allergic individuals and repellents intended for children. The inclusion of natural components (aloe, etc.) into the product encourages the consumer to make a choice in favor of a particular protective agent.

Foreign manufacturers have rather weak position in the markets of Russia and Belarus. All repellents (before getting to shops) undergo mandatory testing in Russian and Belorussian Federal Consumer Rights Protection and Human Health Control Service, where they are checked for efficiency and toxicological safety.

5.4.2 Repellent fiber modifiers

The two most explored, effective, and widespread in agriculture repellents (DETA and permethrin) have been chosen for fibers modification. Lavender essential oil was used as an alternative modifier.

Deet is the chemical compound possessing repellent action (full name *N,N-diethyl-meta-toluamide*, semifluid pasty mass with a strong sweetish smell, white color, water solubility is 1 g/L, melting temperature is 45°C, boiling temperature is 288–292°C). It is a widespread ingredient for preparations to repel blood-sucking insects when applied on skin and clothes. The preparation was developed in the United States in 1946 to protect personnel in areas with a large number of insects.

Permethrin is (3-phenoxyphenyl)methyl ether of 3-(2,2-dichloroethenyl)-2, 2-dimethylcyclopropanecarboxylic acid. The substance belongs to the group of pyrethroids. It is yellow with orange-brown shade and is an easily melting solid substance or viscous liquid. It causes violation of ionic permeability of sodium channels in the membrane of nerve cells of insects (louses, fleas, mites, etc.) leading to a paralyzing effect. When applied on human skin, absorption does not exceed 2%. After entering the systemic circulation, the active agent is quickly hydrolyzed to inactive metabolites that are excreted mainly in urine.

Lavender essential oil (EO) represents a natural repellent which is popular in southern countries as a means of home protection against blood-sucking insects by impregnating bed curtains and mosquito nets with it. Most commonly, the impregnation compounds are prepared by mixing EO with pyrethroids and carbamates [13,14].

Based on the analysis of data taken from literature, physical, chemical, and technological characteristics of the selected substances, the following ranges of repellent substances concentrations in compositions for fibers modification are determined: permethrin 1%–2% by mass; EO 1%–5%; and DETA 15%–30% by mass.

Aqueous solutions of ethyl and isopropyl alcohols were used as components (surface-active with respect to PET) of the compounds being developed.

Three compositions were used to modify PET fibers of the pilot batch: (1) permethrin, ethyl alcohol, water; (2) permethrin, ethyl alcohol, EO, water; and (3) spray repellent “Gardex” (England) which contains DETA.

Optimization of the modifying compositions based on permethrin was carried out by a criterion of obtaining a stable emulsion. The following emulsion compositions were obtained by trial-and-error for subsequent experiments:

(1) permethrin—2% by mass, EO—1%, ethyl alcohol 96%–70%, water 27%;
(2) permethrin—2%, ethyl alcohol 96%–70%, water 28%; and
(3) repellent “Gardex” contained DETA—30%, odorant—1%–2% by mass, the rest is aqueous solution of isopropyl alcohol.

5.4.3 Assessment of repellent efficiency

The determination of repellents’ efficiency is required to implement medical disinfection. In CIS countries there are only three certified testing centers that can conduct such researches competently. The repellent efficiency of the modified PET fibers was assessed in the accredited (GR N POCC RU.0001.516846) testing center of Scientific-Research Institute of Biocides and Nanotechnologies (Moscow).

The methods of testing conformed to the standard in Ref. [15]. This is based on the ability of hungry fleas to jump and stay for a long time on wobbling fiber specimens (bunches of polyester fibers under study were used as specimens). The insectarium culture of rat flea *Xenopsylla cheopis* was used in experiments. Experimental insects were of the same age. A random sampling method was used to select insects.

Yarns (14.5 cm long) were suspended in an olfactometer (an instrument used to measure the sense of smell) which represents a cylindrical chamber with a cylinder coaxially installed in it. A rotating disc was located on the axis of the latter under the upper cover of the chamber. Twenty-four openings were drilled around the circumference of the disc; upper-end-flared glass tubes (internal diameter of not less than 1.5 cm) were installed into the openings. The tubes hung between the walls of the external and internal cylinders.

When carrying out the experiments, bunches of the modified and original (reference) fibers were placed into olfactometer tubes by alternating one reference bundle with three bundles modified by compounds 1–3 (see Section 5.4.2) and then the tubes were closed with plugs. Five hundred hungry fleas were placed at the chamber bottom between internal and external cylinders. Insects were leaving the chamber of the instrument and were distributed across the bundles of fibers. To assure uniform distribution of the insects, the disc was brought into rotation using an electric motor (frequency 10 rpm). After 20 min, the electric motor was switched off, the tubes were quickly taken off the chamber, and the number of insects in each tube was counted. Experiments were performed at temperature of $24 \pm 2°C$ and relative humidity of $58 \pm 2\%$ in triple replication.

The coefficient of repellent action (CRA) of repellent fibers was calculated by the formula:

$$\text{CRA} = \left[\left(A - B\right) / A\right] \times 100\%,$$

where *A* and *B* are quantities of insects on the reference bunch of nonmodified fibers and on the bunches of modified fibers in 20 min after starting the experiment. CRA was determined for newly modified fibers and then the measurements were repeated later in 6, 14, and more days. The results were processed statistically according to method [16].

5.4.4 Manufacturing and properties of repellent fibers

The fibers with repellent properties were obtained by using nondirectional PET fibers, grade A, nominal linear density 0.33 tex, as the raw material.

The temperature of the modifying liquid in a tray of the laboratory bench was 20–25°C. The fibers' travel speed was 4–5 m/min, and the draw ratio 2.3–2.5. The fiber drawing point was found by measuring the fiber diameter at various sites of bundle being drawn. The tray and the bundle-moving rollers were located to ensure that the drawing point was in the liquid. After the fiber had left the tray, it was subjected to thermostabilization by passing through a tube-type furnace at a temperature of 95°C.

Unlike the standard technology of staple fiber processing, PET fibers possessing repellent activity were not subjected to drying in a heat chamber due to the increased volatility of active components of repellent liquids.

When testing the initial nonmodified PET fibers it has been established that the test specimen of newly formed fibers exerts own repellent effect on fleas: CRA = 80.7%. When the same specimen was tested again 10 days later, its own repellent action decreased to 76.7%, and in 14 days (when stored open)—to 27.2%.

At the first test, all fibers modified by compounds 1–3 repelled the fleas completely (CRA = 100%). After 6 days of the fibers' open storage in the laboratory premises, specimens No. 2 (modifiers—permethrin + EO) and No. 3 (DETA) repelled the fleas completely, while for specimen No. 1 (permethrin), CRA was 87.8%. When strips of white coarse calico were taken as reference specimens, CRAs of repellent PET fibers were even higher (after 6 days): specimen No. 1—97.2%, Nos. 2 and 3—100%.

After 14 days of open storage, the repellent specimens displayed the following CRA values (in comparison with the reference PET fibers): No. 1—75.9%, No. 2—79.5%, No. 3—84.3%; when compared to the coarse calico specimens, the values were as follows: No. 1—82.5%, No. 2—85.1%, No. 3—88.6% (Table 5.6).

According to the technique set out in Ref. [15], CRA < 70% is considered to be the loss of repellent activity. Extrapolation in time of the CRA values registered after 1, 2, and 3 months is an evidence of the fact that repellent fibers retain the indicated CRA value for more than a year. This is the confirmation of feasibility of applying the crazing technology to impart the PET fibers with repellent activity.

Table 5.6 **Efficiency of PET fibers repellent action against *Xenopsylla cheopis* fleas**

Specimen no. (modifier)	Frequency	The fibers' repellent action coefficient depending on the specimens' storage time						RAD (days)
		1 day		6 days		14 days		
		Number of fleas on the specimen (pcs)	CRA (%)	Number of fleas on the specimen (pcs)	CRA (%)	Number of fleas on the specimen (pcs)	CRA (%)	
No. 1 (permethrin)	1	0	100%	0	87.8%	0	75.9%	>14
	2			1		5		
	3			0		1		
No. 2 (permethrin + lavender EO)	1		100%	0	100%	2	79.5%	
	2			0		1		
	3			0		2		
No. 3 (DETA)	1		100%	0	100%	1	84.3%	
	2			0		0		
	3			0		3		
No. 4 (control)	1	4	80.7%	2	76.7%	12	27.2%	>6
	2	1		2		7		
	3	0		4		6		
Coarse calico strips	1	7	0%	15	0%	14	0%	0
	2	12		15		11		
	3	16		6		7		
	4	9		12		13		
	5	12		10		12		

RAD, repellent action duration.

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Fibers for securities protection from counterfeit

6

6.1 Methods of securities protection from counterfeit

Despite broad implementation of electronic banking technologies in most countries, the use of cash as well as other protected articles (securities, identity cards, means of product and trademark protection) remains fairly wide. By using modern reprography systems, counterfeiters are seeking ways to reproduce traditional security features. Annual events involving leading state organizations and commercial companies—issuers of banknotes and securities, developers of anticounterfeiting technologies, and equipment manufacturers—underline the rigorous attention being paid to problems of issuance of banknotes, securities, and other protected articles [1]. Currently, security of paper web as the basis for any printing process appears to be the best protection against falsification of products.

Protection from counterfeiting is a complex of protective elements introduced into a valuable security in the process of its manufacture to prevent falsifications and to facilitate counterfeit detection. It entails prevention of all known types of falsification, including the most advanced analog methods. Protection of securities from counterfeiting is assured by the use of special technologies, a certain combination of techniques and methods of polygraphic processes, as well as by the use of special materials. According to the US National Association of Securities and Business Papers Manufacturers, paper web accounts for 70% in reliability of the printed product protection against counterfeiting [2].

Nowadays, hundreds of types of securities and documents with different levels of protection against counterfeit are circulating in the market of paper products. For some documents (banknotes, passports), the level of protection is very high, while for others (receipts or cash receipt orders) it is much lower. It is necessary to have an accurate understanding of the efficiency of various means of protection to determine correctly the level of protection for a specific document.

Indeed, neither method of falsification, but the analog one, is suitable to counterfeit the protected paper web. The original method is practically unavailable to counterfeiters due to huge capital investments in paper production (tens of millions of dollars). The production of protected papers is always controlled by the state, thus any attempt to place an order for the paper counterfeiting is doomed to failure. It is necessary to emphasize that application of any (even the most perfect) method of the paper web protection without the use of other protection methods will not produce the desired result. A combination of different methods is key to success.

The system of document protection is established in the process of planning of its production, starting from development of the original model, selection of

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technological process, materials for paper web manufacturing, printing, etc. A complex of measures for documents protection shall primarily assure inexpediency of their counterfeiting [3].

Paper medium can be protected with watermarks, special types of fibers and threads, confetti, chemical reactionary additives, etc. Three methods are used to protect the following securities [4]:

- technological;
- physico-chemical; and
- polygraphic.

Technological protection is generally understood as a complex of distinctive features discovered at studying the materials which compose the document and, primarily, its paper base. This type of protection includes:

- paper watermarks, security threads (strips);
- security fibers; and
- paper composition and its optical properties, optical properties of dyes, holographic images.

Watermarks are the images formed during the manufacturing process of paper by local variations in its thickness which are visible in transmitted light. It is the most common and reliable type of paper protection. At the same time, it is rather complex as it requires special technological equipment (paper-making machine). All currently known methods of watermark imitation are based on variation of optical density of the ready-made paper.

Security thread is a narrow (1–2 mm wide) strip of polymer material incorporated into the paper during its manufacturing process. At examination of the document, security threads can be seen in transmitted light, as well as reflected diffused and oblique light.

There are two main kinds of security threads with regard to their appearance:

- threads which are located completely in the paper (hereinafter called “latent” for simplicity); and
- diving (window) threads that appear partially on one of the paper surface.

Security fibers are incorporated into the paper pulp during its manufacturing process. They differ from other fibers that actually make up the paper in certain properties: color, shade of luminescence under ultraviolet (UV) rays, sometimes in both of them. Usually the following kinds of security fibers are used:

- colorless fibers which luminesce in UV rays;
- dyed (colored) fibers which have no luminescent glow; and
- dyed fibers which luminesce with “own” color (i.e., the color of luminescence is close to the color of fibers at daylighting) or any another color.

Optically changing (variable) dyes are widely used nowadays as a measure for technological protection of documents. They are usually called Optically Variable Ink (OVI) [2]. This type of protection envisages the use of special ink which can change color in a certain range depending on the angle of light incidence and view.

Usually these dyes are used to apply fragments of images which are performed by intaglio printing: banknote denominations, names of issuing institutions. Currently OVI are used in banknotes, visas and visa coupons, and securities. Practically all modern currencies have this kind of protection.

The *security hologram* is currently one of the most reliable types of protection owing to its high technological effectiveness. Holographic images used as the means of protection are executed by different technologies which have two things in common—large volume of transmitted data and complexity of production. "Classical" holograms are the images made on special foil with several "plans," i.e., different images, including three-dimensional ones, can be seen at different angles of observation. The so-called *kinegrams* which produce an illusion of movement or change in the displayed object geometrical dimensions are one type of holograms.

Paper *optical properties* used for technological protection are visible to the naked eye. Shading (dyeing of the paper pulp to add a certain shade to it) can be primarily related to such properties. When the shading is performed, cloth and mesh marks remain on the paper. This is an indication of the use of a certain paper-making machine: the device used for paper manufacturing (formation).

Physico-chemical protection is imparting the paper with the properties detected in different areas of absorption and radiation spectra. As a rule, these are different kinds of luminescence, ability of absorption, as well as manifestation of magnetic properties of colorants. They are often combined with other types of protection, usually with the technological one. The following kinds of physico-chemical protection are most commonly used:

- luminescence (complete or fragmented) of security threads;
- luminescence of security fibers; luminescence of dyes (colored or colorless);
- magnetic properties of dyes and security threads; and
- application of special colorants (so-called "marks").

Types of protection usually called simply "chemical" ones envisage availability (in the paper structure) of special substances (reagents) or dyes which purpose is to complicate or make impossible any partial change of the initial content of the document (e.g., by etching). When an attempt is made to introduce any change, the paper of the document or dyes used change their properties—usually, they change their color.

Physico-chemical protection, unlike the technological one, can be detected by special devices (and not visually). These devices are divided into two groups: visualizers and detectors (sensors). The first group allows the visual observation of the effect of protection, for example, luminescence of protective element (fiber, thread, image) in UV rays. In addition, it can be represented as a pattern of UV rays absorption or magneto-optical visualization of the colorant properties. Devices of the second group operate based on a yes-or-no principle, i.e., they react on protection feature availability by giving a sound or light signal.

Luminescent protection is glowing of protective elements (fibers, threads, colors) excited by the sources of UV rays in different ranges of this spectral band. Sources of radiation with wavelength of 365 and 254 nm are the most frequently used ones in actual practice. Such devices can be made in the form of portable light sources ("flashlights") or can be incorporated into stationary instruments.

Luminescence is provided by special substances (luminophores) which are incorporated into the materials composing the document. There is a very wide range of such substances, and there are various colors of luminescence, most commonly blue, yellow, green, and red.

Infrared protection is based on properties of materials which a document is composed of (most often, colorants) to differently absorb or pass infrared (IR) rays. There is a rather large number of "domestic" devices to determine the luminescent protection; however, for identification of IR protection. special devices (generally used only by experts) are required.

Starting from 1999, all US dollar banknotes include an element of IR protection in the backside image: a certain combination of transparent (invisible in IR rays) vertical strips, and this combination is individual for each banknote nominal value. Similar protection is used on Euros, but in this case the localization pattern (IR contrast) is more complex.

Magnetic protection assumes that the materials (which the document is composed of) possess magnetic properties. Colorants are the most common of them, but sometimes magnetic properties of security threads are used for protection.

There are two types of colorant-related magnetic protection. The first type assumes the availability of magnetic properties of any document's requisite, usually its serial number. Most banknotes in circulation, certain securities, and other types of documents have this kind of protection. Magnetic protection of the second type envisages local distribution of magnetic properties within the image.

It is generally assumed that the means of the printed matter protection are a totality of printing techniques and methods (polygraphic technologies) which defines properties of the image visible in the document. Specific features of two types are formed when using such means, including:

- actual features of the printing methods which are normally determined visually or by using the simplest devices, e.g., a magnifying glass; and
- special effects which appear due to the use of a specific technology and are usually detected by other methods (in oblique lighting, by touch, etc.).

Chemical protection of the paper web surface is exercised by introduction of special additives. This method is a high-tech one and serves two purposes [5]:

(1) paper web protection (and a polygraphic image, respectively) against chemical etching;
(2) identification of paper web authenticity.

The chemically protected paper primarily performs only the second protection function or, upon the request of the task originator, both of them.

Counterfeiters often use chemically active reagents for etching a polygraphic image. Chemical protection of the paper web is intended to prevent such counterfeiting. A layer of dyeing microcapsules coated with the masking cover is applied on the paper surface layer. The capsules cannot be seen visually on the paper surface. The capsular layer represents a blend of coarse particles, where each type of capsules is dissolved under the influence of an individual chemical reagent contained in the chemical composition used for etching. The coloring capsule coating is dissolved under the action of the chemical reagent, and the paper web is dyed (in the place of the influence) with permanent spots varied in color. Availability of such a spot is clear evidence of erasure. Each dyeing capsule, under the influence of the corresponding reagent, colors the paper with a specific color. The manufacturer provides the customer with a test table of color reactions of chemically protected paper.

The current protection of the paper web authenticity identification is based on the principle of the web reaction (with certain color) on a specific reagent. If a complex chemical protection of the paper against etching is applied, it is also an identifier of the paper authenticity. After the paper is exposed to certain reagents, its color reaction is compared against the test table. Compliance of color reactions means that the paper is authentic, while noncompliance or lack of such reactions is an indication of counterfeit.

When the complex chemical protection against etching is not necessary, an identifying chemical protection of paper authenticity is used. To this end, the finely dispersed microcapsular coating which reacts with certain color to the specified chemical reagent is used. In particular, such protection is used in US dollars, for which reason special tester markers are manufactured to check the banknotes' authenticity.

Chemical protection of the paper web can be effectively used in both controllable and uncontrollable environments as the explicit and implicit form of protection.

In terms of the etching detection, complex chemical protection may well be an explicit protection which does not require high skills for counterfeit identification: the user is not required to identify a type of chemical reagent, it is sufficient to see a bright color spot in the paper which in itself raises suspicions. This method of protection can work effectively in the conditions of uncontrollable environment. Complex chemical protection is an effective method of identification of the paper web authenticity in the professional environment and in the form of implicit protection.

The web protection with homogeneous layer of capsules for elementary identification of the paper authenticity is very effective and can act both as implicit and explicit protection in the conditions of a simply controlled environment and availability of elementary test tools (marker testers). If this method of protection is chosen, it is necessary to take into account that the microcapsular layer (although it is invisible) reduces whiteness of the paper web compared to the base paper without microcapsular coating. The whiteness of the paper with microcapsular layer does not exceed 89% ISO.

When choosing a technology for printing on the paper with chemical protection, the use of alcohol-containing wetting solutions in the printing machine should be avoided. Such wetting may have an adverse effect on the condition of microcapsular layer (including its destruction).

Counterfeit of the paper chemical protection is theoretically possible; however, such precedents are not known. Such falsification is incredibly expensive, and the counterfeit itself suggests a high level of professionalism and a complex of scientific and technical researches.

6.2 Paper filling with threads and fibers

Security thread is a narrow (1–2 mm wide) strip of polymer material incorporated into the paper during its manufacturing process. At examination of the document, security threads can be seen in transmitted light, as well as reflected diffused and oblique light [1]. Two main kinds of security threads can be distinguished with regard to their appearance:

- threads which are located completely in the paper (hereinafter called “latent” for simplicity); and
- diving (window) threads that appear partially on one of the paper surface.

The latent threads are visible in transmitted light only. In turn, they are subdivided into the following options:

- metalized solid threads which are viewed as a nontransparent strip;
- metalized with text, in the form of a nontransparent strip with transparent (light-faced) letters and numbers; and
- transparent with text, semitransparent strip with nontransparent (dark) symbols or images.

In addition, metalized threads can possess magnetic properties. Transparent threads sometimes luminesce when viewed in UV rays. These properties may be manifested over entire length of the thread and locally.

Diving threads may be seen in the transmitted and reflected light. As a rule, they are metalized; therefore, in the reflected light, the thread is seen as a dot line consisting of lucent pieces of equal length on one of the sides of the document while the same thread represents a solid strip when viewed in transmitted light. Technologically, the diving threads are divided into the following types:

- solid, where no text or images are seen when viewed in the transmitted light;
- with the transparent text; and
- with a holographic effect, i.e., the ones with “iridescent” coating.

An additional degree of protection is provided by local changes in the paper optical density in the form of dark strips (perpendicular to the thread) which are seen in the transmitted light in the area of the diving thread location. These strips are visible between the coming-to-the-surface sections of the thread.

In the oblique light, local thickening of paper (which looks like a textured strip) is observed in the areas of location of all types of security threads.

Security fibers are incorporated into the paper pulp during its manufacturing process. They differ from cellulose fibers that actually make up the paper, primarily in their nature (most often they are synthetic fibers), as well as in specific properties: color or shade of luminescence in UV rays, or sometimes both. Usually the following kinds of security fibers are used:

- colorless fibers which luminesce in UV rays;
- colored fibers which have no luminescent glow; and
- colored fibers which luminesce with “own” color (i.e., the color of luminescence is close to the natural color of fibers) or any another color.

Security fibers of one or several types may be encountered in documents. They are usually located in the paper pulp, but can partially (and sometimes completely) protrude from its surface.

Colorless security fibers are not visible under normal viewing conditions. Occasionally, they may have a color shade, most often yellowish or greenish. Luminescence of such fibers is observed at illumination with UV rays.

Imitation of security fibers has the following features. Usually, counterfeiters pay less attention to security fibers at falsification of documents. Imitation of the dyed fibers is performed, most often, through simple, accessible means: hand-drawing; overprint; sticker (which is rare). In cases when the fibers are imitated by hand-drawing, their appearance depends on the tool that was used for their execution. For example, the use of a color pencil results in a "puffed" picture, stroke thickness is pressure-sensitive, traces of pressure are visible. In the "fibers" applied with a ball felt-tip pen (roller), a color "dump" is usually visible—stroke edges have a more intense color.

6.3 Luminescent colorants for fibers

Introduction of chemical fibers dyed with fluorescent colorants into the paper base structure has proven to be an efficient method of protection. The advantages of this solution are simplicity of paper identification and complexity to manufacture a counterfeit which looks like the original [3].

The luminescent dyes are characterized by glowing which exceeds their thermal radiation under the given temperature and excited by any power source (UV, IR, radioactive, X-ray emission, etc.). The most common brands of *luminescent colorants* produced by chemical industry are the following [6–8]:

Rhodamine C (chemical formula: $C_{28}H_{31}ClN_2O_3$). It is a crystal powder of gray-brown color with green shade. It dissolves well in ethanol, chloroform, acetone, dimethyl formamide, and water. Luminescence in solid state is claret-colored; in solution it is salmon pink.

Fluorescein ($C_{20}H_{12}O_5$). It is a crystal powder of yellow-orange color. It dissolves well in dimethyl formamide, chloroform, ethanol, and acetone; it is insoluble in water. Luminescence in solution is yellow in color.

Eosin ($C_{20}H_4Br_4Na_2O_5$). It is a crystal powder of dark red color. It dissolves well in dimethyl formamide, water; partially in acetone and ethanol. It luminesces in solution with a yellow-orange color.

Neutral red ($C_{15}H_{17}ClN_4$). It is a crystal powder of dark green color. It dissolves well in chloroform, ethanol, and water; it dissolves partially in acetone and dimethyl formamide. Luminescence in solution is red in color.

Powdered dyes for synthetic fibers are used as compositions of basic colorants, and they differ in their properties from the dyes of industrial and domestic use.

In some cases, *luminophores*—organic substances luminescent under the influence of external power sources—are introduced into the structure of synthetic security fibers and paper base (marks) [9].

Thermochemical luminophores change their color at the change of temperature. Heating up to the color-transition temperature is a detector which reveals a thermochromic mark on the paper. When cooling, the mark color returns to the initial state (reversible thermochromic pigments).

Cryoluminophores are substances where luminescent properties are manifested at subzero temperatures. According to their chemical structure, they are complexes of europium (turning red when cooled) or terbium (turning green when cooled).

Antistokes luminophores are excited by IR light. They are inorganic compounds of Y_2O_3 type. They emit green light at excitation. They cannot be determined by chromatography since they are not soluble in organic solvents.

Photochromic compounds are colorless, but when irradiated with UV light (365 nm) they acquire a color in the range from red to blue, which disappears in the dark when illuminated with red light or slightly heated.

Thus, an extensive nomenclature of photoactive agents is developed to manufacture luminescing synthetic fibers and security "marks" on the paper base. They can be used to impart different levels of protection to documents. The choice of an active agent is determined by technical and economic criteria which are not identical in different countries.

6.4 Requirements to fibers and methods for their production

Security fibers are short pieces of fiber up to 10 mm long. They are introduced into the paper base in the process of its manufacture; they can be chaotically distributed in the cellulose pulp or represent a strip 3–4 cm wide [5]. Special properties are imparted to chemical fibers which allow the implementation of additional elements of protection.

Fibers can be *colored* or *uncolored* with a diverse color palette. The fibers processed with luminescent colorants considerably enhance the level of protection of documents. *Luminescent* fibers can be colored and colorless at daylighting. When security fibers of different colors are introduced into the structure of the paper base for documents, addition of three types of fibers which differ in fiber color at daylighting or in its luminescence under the influence of UV radiation is considered sufficient. It is not advisable to use fibers with blue luminescence as they are easier to forge [3]. Security fibers with discontinuous coloring, for example, *two-color* ones which look unicolored (although alteration of colors is visible under magnifying glass), are considered to be the most effective.

Profiled security fibers are distinguished by a specific form of cross-section obtained in the process of formation. They can be easily identified, have relatively low cost and cannot be counterfeited by polygraphic or other methods.

Experts of the Federal State Unitary Enterprise Goznak, Russian Federation, have developed the so-called *graded* fibers ("Zone" fibers) with variable diameter in which areas with various cross-sections are alternating. Such fiber may contain alternating colored and uncolored, luminescing and passive in UV range sections [5].

Bicomponent fibers having different optical properties along the transverse direction are developed and applied. Such fibers are formed from the melts of blends of limitedly compatible or incompatible polymers (copolymers) [10]. Fibers with additional special properties, for example, by imparting *ferromagnetic* properties to them, are produced to increase the level of protection.

In Belarus, the requirements to security fibers are regulated by the Instruction on production of forms of strict reporting and special materials [11]. Security fibers shall have the following properties:

- visible luminescence which is controlled visually or by using special devices (ultraviolet, infrared radiation, etc.);
- optimal length of 3–6 mm;
- thickness of an individual fiber should not exceed thickness of the paper which it protects; and
- heat-resistance at temperatures up to 140°C.

The properties of chemical fibers which determine the level of securities protection, primarily, reliability of the colorant and other security elements binding to the fiber, are formed in the process of manufacture and target modification of the fibers.

Synthetic fibers are dyed by filling the melt or polymer solution with the dispersed particles of the dye. This method is usually used to manufacture fibers of black color. To produce fibers of other colors, as a rule, solutions of organic dyes are used. Polyester fibers are kept in the dye-bath at $T = 50–55°\text{C}$ for 2–5 min [12]. The range of organic dyes is very limited, and one-color fibers obtained with the use of such dyes have pale color and are insufficiently effective for protection of documents from counterfeit.

The improved variant of the method envisages the processing of newly formed threads in a bath with the aqueous solution of the dye in two stages. At the first stage, dyeing is performed at $T_1 = 100°\text{C}$ by drawing the threads through the bath at a low constant speed. At the second stage, the temperature is increased to $T_2 = 105°\text{C}$ and drawing speed by 1.5–10 times [13].

There is a known method of dyeing with liquid colorant which is applied to the surface of fibers by spraying under pressure from a nozzle. The dye is randomly distributed along the fiber; it is rather difficult to adjust its amount and hue [14].

Dyeing of the fiber at local areas allows a considerable increase in the level of protection. One method for such dyeing envisages production of twisted yarn from the fibers which is then painted and cut into short pieces [15]. The staple fiber thus produced has alternating colored and uncolored areas and can be dyed again with another colorant. Limitations of this method are high level of labor input, lack of clear-cut distinction between the areas, and impossibility to regulate the length of the dyed areas.

At discontinuous dyeing of fibers according to method [14], a colorant and activating liquid are used. First, individual areas of fibers are charged by applying unipolarly charged particles of activating liquid to them. Then, the fibers with charged and uncharged areas are placed into the colorant and areas with different intensity of coloring are obtained. Flexible control over dyeing is exercised through a computer. This method allows the automation of the dyeing process and the accurate dispensation of the drops of activating liquid.

The technology for dyeing chemical fibers with the vapors of colorants is rather new. The vapor-phase technology of dyeing is implemented by converting the colorant into sublimated state from which the colorant vapor is adsorbed by the fiber surface. Color intensity depends on the speed of the thread passing through the dyeing chamber (intensity is higher at lower speeds) [16].

The considered methods of dyeing assure application of the colorant on the surface of fibers, so the color stability depends to a large extent on thermodynamic affinity of the dye with the fiber material.

The use of the crazing technology is a promising method of synthetic fibers modification with dyes or other target additives.

At dyeing by crazing mechanism, fiber is exposed to drawing in surface-active liquid medium containing coloring matter. Such technology allows giving stable coloring to achromatophilous polyester fibers, it being highly productive and easily fitting in the standard process of manufacturing chemical fibers without requiring considerable modification of technological equipment [17].

The structure of fibers exposed to dyeing in the process of crazing has been investigated by the method of atomic-force microscopy (AFM) with NT-206 device (Microtestmachine Co., Belarus) [18].

Fig. 6.1A shows a "slammed" craze profile, its depth being about 0.2 µm. It does not mean that coloring agent penetrates exactly to such depth. Fig. 6.1B demonstrates REM image of a lateral shear of dyed fiber where one can see that the depth of

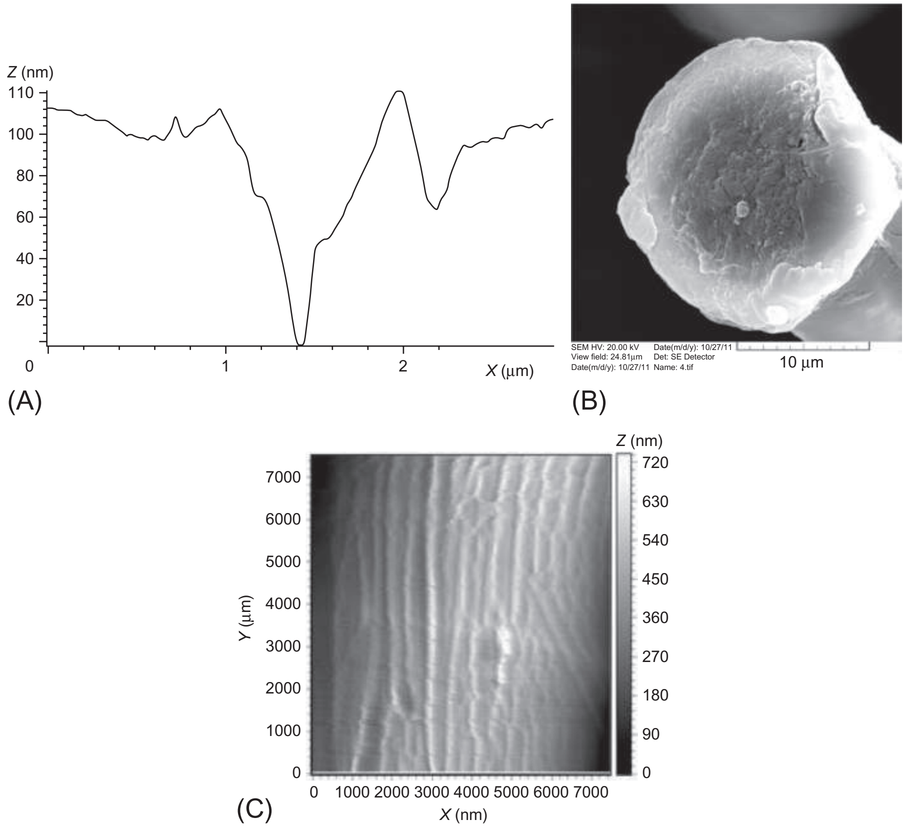

Fig. 6.1 Structure of PET fiber dyed by Rhodamine coloring agent: (A) craze profile, (B) lateral shear of fiber, and (C) fiber surface.

penetration of luminescent coloring agent (it luminesces under electron beam impact) is at least two degrees higher.

One can imagine that coloring agent penetrates to the whole depth of an opening craze (200–250 µm) and even deeper—at the expense of diffusion. In the process of relaxation of stretching strains in fiber (zone IV in Fig. 2.1 from Chapter 2) craze walls clamp. Particles penetrated into crazes do not let the walls interlock completely. Craze profile in Fig. 6.1A fits just this situation. Fibrillization of superficial layer of fibers at stretching (stretching ratio $\varepsilon^* \geq 3.0$) causes fibrillar formations yielding on fiber surface and forming specific corrugations-shaped texture registered in Fig. 6.1C by AFM method.

6.5 Discontinuous dyeing of fibers

In the United States and Russia, the securities are made by using the paper base filled with synthetic fibers with discontinuous dyeing. Each piece of the fiber has areas dyed in two and more colors alternating on a piece of very small length of 0.3–1.5 mm [19].

We have developed a rather simple device which allows the production of discontinuously dyed polyester fibers [20].

The device (Fig. 6.2) consists of two sets of the fiber-drawing rollers, the first set of rollers rotation speed being lower than the other one. A toothed roller is installed between the sets of drawing rollers. Its axis is perpendicular to the direction of movement of the bundle of fibers being modified, and the teeth pitch is equal to step of alternation of the modified and nonmodified fiber areas. The teeth of the fiber lower part are in contact with the surface-active modifying liquid, while the bundle of fibers rests upon the upper teeth. The toothed roller is brought into rotation at frequency

$$\gamma = v / \pi d,$$

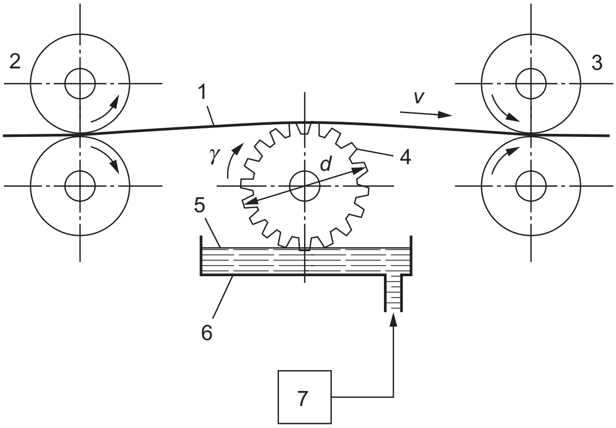

Fig. 6.2 Diagram of the device for discontinuous dyeing of fibers: 1—bundle of fibers; 2, 3—sets of rotating rollers; 4—toothed roller; 5—modifying liquid; 6—bath; and 7—liquid level control system.

where v is linear speed of fibers travel by drawing rollers, d is the diameter of toothed roller around the tops of teeth.

To apply the modifying liquid on the fibers with the given accuracy, the linear speed of the tops of teeth travel should be equal to the travel speed of the bundle of fibers drawn by the rollers: $\nu = \pi d \gamma$, i.e., $\gamma = v / \pi d$. When the teeth of the fibers are wetted with the modifying liquid, a layer of liquid is formed at their tops which is transferred to the fibers' bundle pulled by the drawing rollers. The fiber areas wetted with the modifying liquid alternate with the "empty" areas. At sufficient draw ratio of the fibers, the crazes are formed only in the areas which are in contact with the tops of teeth. As a result, the fiber acquires discontinuous texture in the mode of rational use of expensive modifier, such as, for example, luminescent dyes.

The device works as follows. The drives of drawing roller sets (2 and 3) shall be switched on. Due to difference in rotation speeds, the bundle of fibers 1 is drawn to the degree sufficient for initiation of crazes, and it moves from left to right with speed v. It rests on toothed roller (4) which rotates with frequency γ so that linear speed of the tops of its teeth travel is equal to v. The teeth of the roller (4) in a low position are wetted with a modifying liquid (5). When (during the roll rotation) these teeth come into contact with the bundle of fibers 1, a layer of the modifier is transferred to the fibers. An array of areas wetted and nonwetted with the liquid is formed on the fiber. The liquid penetrates the crazes and after the bundle has come out of the set (3) of the rollers, it remains in the fiber areas which had contacted teeth of the roller (4). The length of the modified areas equals to the length of the tooth top and the modified areas alternate with the nonmodified ones which length is equal to the distance between tops of teeth. The system (7) maintains constant level of the modifying liquid in the bath (6), and despite the liquid entrainment by the roller (4) it ensures long-term operation of the device.

An original device has been used for discontinuous modifying of chemical fibers by crazing mechanism [21]. It contains two sets of withdrawal rollers for transporting and stretching of fibers, the first sets of rollers rotation speed being lower than the other's. The last roller of the first set has been made toothed with teeth spacing equal to the length of dyed fiber segment. The contact zone of toothed roller with counterbody, which is a conjugated smooth support plate, is in the bath and is dipped into surface-active liquid containing coloring matter. The bath bottom is coated with an elastic covering.

The drawing point of the modified fiber, at which generation of crazes starts under proper degree of drawing and dampening by surface-active liquid, is at the exit of fiber from "toothed roller/counterbody" contact (Fig. 6.3). When the fiber is pressed to counterbody tooth by force F_1 (Fig. 6.3A), the degree of drawing is maximal and sufficient for initiation of crazes, therefore fiber segment at exit from contact is dyed due to capturing coloring agent by crazes. When slipping along the counterbody, the fiber is between the teeth (Fig. 6.3B, force F_0), and the degree of its drawing is lower than is necessary for craze initiation. As a result, the fiber segment between positions where the fiber was pressed to the counterbody by adjacent teeth remains undyed.

The experiments were carried out with nonoriented polyethylene terephthalate (PET) fibers of nominal linear density 0.33 tex mark A of Mogilevkhimvolokno Co. (Belarus) production. To treat the fibers, solutions in isopropyl alcohol (propanol-2) luminescent coloring agents—Phenalemine-160, Oxazine-17, Rhodamine-C,

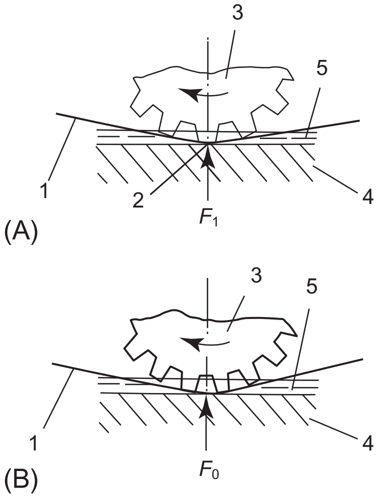

Fig. 6.3 Scheme of interaction of fiber and toothed roller at discrete modifying: (A) fiber is pressed to bath bottom, (B) fiber is between teeth. 1—fiber, 2—drawing point, 3—toothed roller, 4—bath bottom, 5—surface-active liquid.

Fluorescein, Eosin-H, and EK-3FP mark colorant—have been used. Dyed fibers have been investigated in UV light with "Peleng VK-04" designed to control documentary stamps (included in Belarus Public Register of Equipment to check identity of securities and documents).

It has been determined that at stretching ratio $\varepsilon^* = 2.5$ (corresponds to specific elongation $\varepsilon = 250\%$) fibers modified by Phenalemine solution have the lowest glow intensity. The effect of polarization division of luminescence in such fiber is near to similar indicator of original fiber. Other coloring agents noticeably exceed Phenalemine by glow brightness. Oxazine is distinguished by high brightness. Fibers dyed with it which are practically clear in visible light acquire coloring in UV light (Fig. 6.4). EK-3 FP colorant causes the most intense glow in UV radiation.

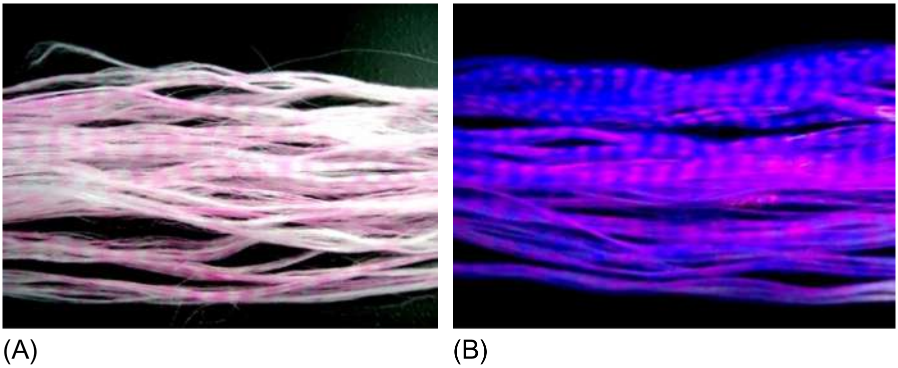

Fig. 6.4 The view of PET fibers discretely dyed by Oxazine: (A) in visible light and (B) in UV light.

In the result of by-turn modifying by two fluorescent coloring agents, a fiber with the effect of alternating polarization division of colors has been obtained: areas of orange-pink and purple colors. The fiber was first evenly dyed (at $\varepsilon^* \approx 2$) by EK-3FP coloring agent solution, then exposed to discontinuous dyeing (at $\varepsilon^* = 2.7–3.0$) by Oxazine solution. Choosing combinations of coloring agents differing by glow color in UV radiation, it is possible to give fibers set alternation of colors implementing a planned scheme of protecting paper filled with fiber bits.

A similar task for discontinuous dyeing of the fibers was solved by using a device [22] of which the operating principle is shown in Fig. 6.5.

The device (Fig. 6.5A) consists of sets of rollers (1 and 2) which rotate at frequencies $n_1 < n_2$. A pair of adjustment rollers which is formed by backing roller (3) and mating eccentric roller (4) is located between them. It is brought into rotation at frequency n_3 in the direction opposite to the movement of roller (5) from set (1). Bundle (6) of the fibers being dyed passes through the set (1) rollers, between rollers (3) and (4) of the adjustment pair and is captured by the set (2) rollers. Fluid nozzle (7) which is connected to a device for pumping the surface-active dyeing liquid is installed above the area where bundle (6) leaves the roller (5). Eccentricity e of roller (4) corresponds to thickness h of the bundle of fibers being dyed.

The device works as follows. Set of rollers (1, 2) and eccentric roller (4) are brought into rotation. The fibers' bundle (6) moves toward the set (2) rollers and is subjected to drawing. Hydraulic system for the dye pumping into nozzle (7) is enabled, and jet (8) of the surface-active dyeing liquid is sprayed onto the fibers in the area where the

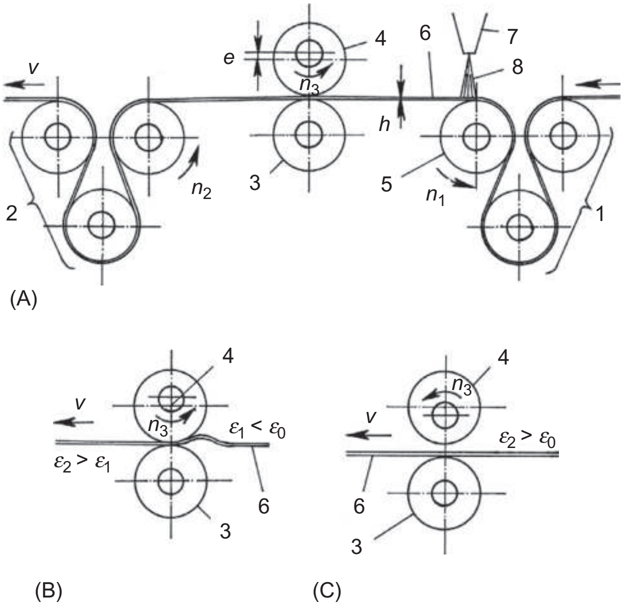

Fig. 6.5 Device for discontinuous dyeing of fibers: 1 and 2—sets of rollers, 3 and 4—pair of adjustment rollers, 5—roller, 6—bundle of fibers, 7—nozzle, 8—fluid jet.

latter leave roller (5). It is the area of the fibers' "drawing point" where (under the corresponding conditions) the craze initiation begins.

Rotating eccentric (4) can be located in two extreme positions with respect to backing roller (3). When the eccentric presses the bundle of fibers (Fig. 6.5B) to roller (3), the fibers are drawn [between rollers (3 and 5)] with ratio $\varepsilon_1 < \varepsilon_0$, where ε_0 is the minimum draw ratio for the fibers of the given type under which the craze initiation begins. In the area of leaving roller (5), the fibers are wetted with jet (8) of the surface-active liquid, however the crazes are not formed and fibers are not dyed. In Fig. 6.5C, eccentric (4) does not touch the fibers' bundle (6). The fibers are drawn over entire length of the bundle with ratio $\varepsilon_2 > \varepsilon_0$ which is defined by the ratio between the rotational speed of rollers of sets (1) and (2). In the area where the fibers come out of roller (5), crazes are initiated in them; these crazes capture the dye from jet (8) and the fibers acquire coloring.

Dyeing/nondyeing cycles are alternating n_3 times per time unit (n_3 is the frequency of eccentric rotation). At the fiber speed v, the total length of adjacent dyed and undyed areas of the fiber is $l = v/n_3$.

To dye a fiber for the length of about 1 mm (actually, these types of fibers are used for protection of securities) frequency n_3 of the eccentric rotation has to be very high. It can be significantly decreased when the second option of the invention is used. A toothed roller is mated with backing roller (3). The fibers are dyed when "gaps" between teeth are located over bundle (6), while the undyed areas are formed when the bundle is pressed (with a teeth) to the backing roller. In this case, the dyeing cycles will be alternating $n_3 \cdot z$ times per time unit, where z is the number of teeth of the toothed roller. Total length of adjacent dyed and undyed areas of the fiber is $l = v/(n_3 \cdot z)$. Length of dyed areas of the fiber and gaps between them can be set by using special toothed wheels. They are made with nonuniform distribution of tooth pitch and width corresponding to the required distribution (along the length) of the dyed and undyed areas of the fiber.

6.6 Luminescence of dyed fibers

Luminescence spectra have been obtained [23] with a space-saving spectrometer with the CCD-ruler method of recording. With small overall dimensions, the device enables 0.3 nm resolving ability and has sensitivity making it possible to register luminescence spectra of organic dyes solutions in concentrations up to 10^{-10} mole/L. The effective range of the spectrometer is 400–820 nm. The excitation source of luminescence spectra is either 405 nm wavelength semiconductor laser or 37 nm wavelength gas laser. The spectrometer is run by the computer and has simple and handy software.

The main units of the appliance are optical system, CCD camera photo-receiving component and camera and computer information input control board.

ILX-511 CCD ruler (Sony) has been employed as photo detector. It consists of 2048 elements, their size being 14 × 200 μm. Modes of operation are defined by the program, accumulation time being from 10 ms to 50 s.

Diffusely scattered radiation from light source is coming through a body entrance slit into a collimator lens, where it is transformed into a parallel light beam. The received beam is reflected by a deflecting mirror, goes through the cuvette with material under investigation or fixed fiber bundle; it is then brought together by a camera lens and supplied onto a CCD camera photo-receiving component. Inside the spectrometer's body under the bottom plate, there is the board by which camera and computer information input control is exercised.

To approximate data characterizing luminescence spectra of dye solutions, the least-squares method which makes it possible to achieve high precision approximation and Fourier filtration have been used. The latter has been widely employed by spectral analysis for cleaning signal from noise and smoothing spectrum. Data processing has been performed with Statistica v.6.1 and OriginPro v.7.0 programs.

The degree (ratio) of fiber drawing affects modifying substance sorption [24]. Fiber deformation on drawing from 50% to 250% leads to increasing the amount of dye captured by crazes. On reaching the degree of drawing $\varepsilon^* = 3.0–3.5$ (i.e., $\varepsilon = 300\%–350\%$), when crazes collapsing and transition from loose fiber structure to tight one starts, the inverse process begins—dissolving agent is squeezed out of crazes. Distances between fiber fibrils in the process of drawing continually decrease and eventually become comparable with the sizes of dye molecules. As a result, peculiar ultrafiltration of dye solution occurs at a molecular level, which leads to dye molecules being captured by fiber structure, mainly pure dissolvent being filtered into a bath. To obtain a totally oriented sample, the degree of drawing must be 3.8–4.5 [17].

Thus, more intensive craze formation takes place at drawing ratio ε^* within 2 and 3. At drawing ratio $\varepsilon^* < 2$, fiber surface does not capture modifying substance in sufficient amount while at reaching drawing ratio $\varepsilon^* \approx 3$, crazes are filled with modifying particles at most and adsorption of a large quantity of particles is impossible.

To investigate dye concentration in modifying liquid impact on luminescence intensity, spectral characteristics of Rhodamine solutions at 0.05–4 g/L dye concentration and fibers modified by it have been studied. As dye concentration increases, not only luminescence intensity of the solutions changes, but also their spectral characteristics (Fig. 6.6). Composition with Rhodamine concentration 0.1 g/L (spectrum 2) possesses the most intensive luminescence. With further dye concentration increasing, concentration quenching takes place and luminescence maximum shifts to long-wave spectral region. Luminescence intensity is low and changes insignificantly at dye concentration higher than 1 g/L.

When modifying with luminescent dyes as dye concentration grows in the solution, fibers luminescence color changes from pink to reddish-orange. At the same concentration of dye in the solution, luminescence spectra of dyed fibers (Fig. 6.7) differ markedly from luminescence spectra of dye solutions (Fig. 6.6). The reasons of differences between spectra have been different aggregative states and light refraction coefficients of luminescent media. In addition, the difference between spectra of dye solutions and luminescent fibers, in our opinion, is stipulated by the presence of the original fiber's proper luminescence. One can assume that when treating fiber with dye solution, overlapping of dye luminescence band on long-wave edge of fiber luminescence band occurs. In connection with this, dyed fibers luminesce in a broader

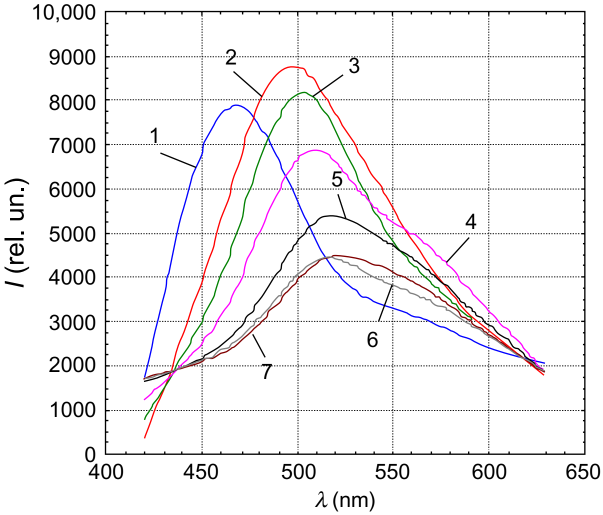

Fig. 6.6 Luminescence of Rhodamine solutions in propanol at dye concentration: 1—0.05 g/L; 2—0.1 g/L; 3—0.2 g/L; 4—0.5 g/L; 5—1 g/L; 6—2 g/L; and 7—4 g/L.

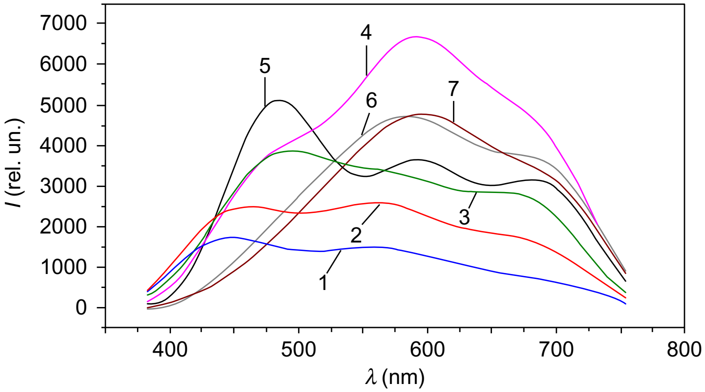

Fig. 6.7 Luminescence of fibers treated by Rhodamine solutions in propanol at dye concentration: 1—0.05 g/L; 2—0.1 g/L; 3—0.2 g/L; 4—0.5 g/L; 5—1 g/L; 6—2 g/L; and 7—4 g/L.

spectral band than dye solutions. As concentration is increased, luminescence maximum of dyed fibers shifts from blue to red spectral region. Fibers treated with composition containing 0.5 g of dye per 1 L of isopropyl alcohol solution have maximal luminescence intensity.

The dependence of luminescence intensity of dye solutions and fibers treated by them is of nonlinear character (Fig. 6.8). The higher dye concentration is in the solution the larger number of dye molecules is absorbed in superficial layer of fiber (curve 2). Concentration quenching of luminescence of fibers begins happening at their treatment by solutions with dye concentration exceeding 0.5 g/L. The optimal

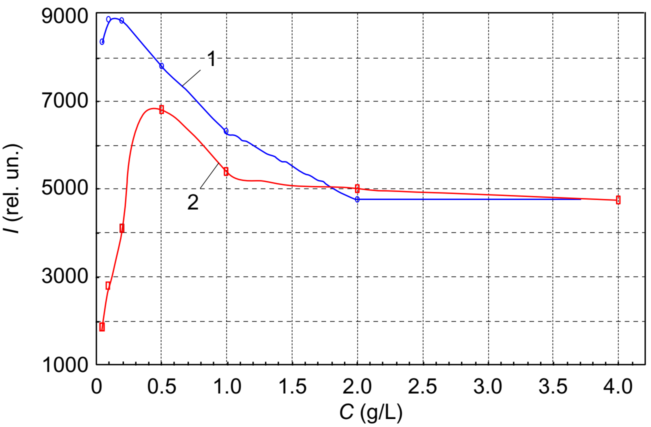

Fig. 6.8 Dependence of luminescence brightness on dye concentration: 1—in solutions and 2—in dyed fibers.

concentration of dye in the solution for dying fibers on the assumption of data of Fig. 6.8 should be considered as 0.4–0.5 g of dye per 1 L of solution.

The luminescence spectra of fibers modified by different kinds of dyes are shown in Fig. 6.9. Luminescence intensity of these fibers increases in the range of

Phenalemine → Fluorescein → Eosin → Rhodamine → Oxazine,

while luminescence intensity of used solutions grows in another order:

Phenalemine → Fluorescein → Oxazine → Rhodamine → Eosin.

One can assume that overlapping of dye solutions spectra on luminescence spectrum of polyester fiber leads to luminescence maximums shifting to red spectral region, luminescence band widening.

Fibers treated by Oxazine and Rhodamine are characterized by the same color and glow in UV light, only pink tints are different. Peculiarity of fibers treated by Fluorescein and Eosin is in the fact that these fibers' colors are different at daylight and exposure to UV radiation. In our opinion, both types of fibers can be employed for protection of documents from counterfeit together or in combination with other types of protective fibers as the standard requirements regulate the necessity to incorporate no fewer than two varieties into paper pulp.

Fibers modified by Rhodamine (Fig. 6.9, curve 1) have luminescence maximums in red, purple, and blue ranges of spectral regions which stipulate bright orange-pink color of glow.

Fibers dyed by Phenalemine (curve 2) have the least intensity of glow, it being complicated to distinguish clear maximums corresponding to any particular spectrum section. In UV light they have pale lilac-pink coloration.

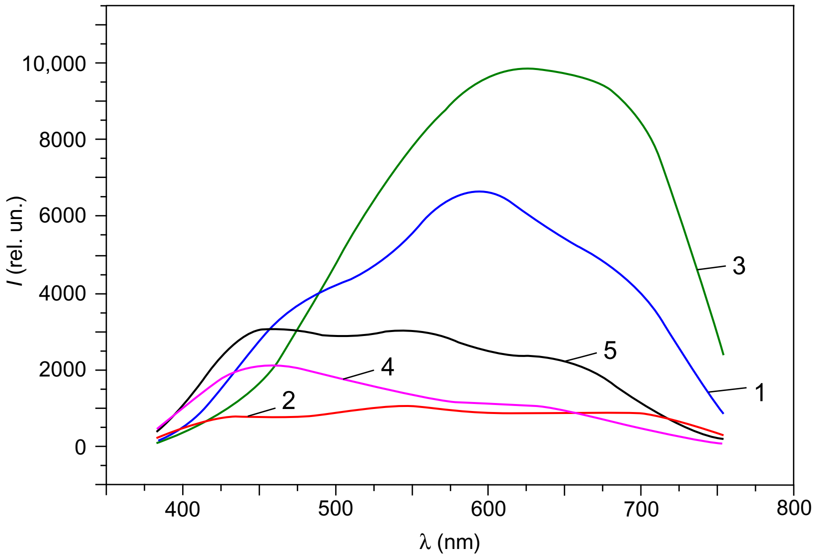

Fig. 6.9 Luminescence of fibers treated by dye solutions in propanol at dye concentration: 0.5 g/L: 1—Rhodamine; 2—Phenalemine; 3—Oxazine; 4—Fluorescein; 5—Eosin.

Fibers treated by Oxazine (curve 3) have luminescence maximum approximately in the same region as fibers modified by Rhodamine. Luminescence intensity of these fibers is the highest compared to other samples; the color of the glow is reddish-pink.

Fluorescein (curve 4) gives luminescence maximums in yellow and blue ranges of spectral regions which stipulate a yellow-green color of the glow. Eosin (curve 5) gives fibers a dim pinky-orange color of glow in UV rays.

Out of examined variants, fibers dyed by Phenalemine are less efficient for protection documents from forgery, since they are distinguished by low intensity of luminescence compared to other fibers. More reliable protection of documents will be provided by fibers treated by other kinds of dyes, especially by Oxazine and Rhodamine, which supply intensive luminescence of fiber in UV radiation.

Thereby it has been demonstrated that intensity and glow color of fibers significantly depend on kind and concentration of dye in modifying solution. Fibers with Oxazine dye have shown the highest intensity of glow with bright red color among all types of investigated fibers. They give maximum of luminous intensity on the spectrum of luminescence in the region of wavelength 620–700 nm, which corresponds to red light. Fibers with other investigated dyes have lower luminous intensity and their corresponding intensity maximums are shifted to shorter wave region. Correspondingly, the color of their glow ranges from orange to green.

It has been determined that dye concentration in modifying liquid affects luminous intensity of fibers in UV light and even (to some extent)—the color of glow. It has been shown with Rhodamine example that fibers modified by solution with dye content 0.5 g/L have the highest luminous intensity (brightness). The reduction of dye concentration results, in the first place, in sharp decrease of luminous intensity of fibers and, secondly, in some shifting of intensity maximum on the spectrum to shorter wavelength, i.e., from bright red to yellow and yellow-green. The increase of dye concentration higher 0.5 g/L practically does not influence the color of fibers glow, but slightly decreases its intensity.

6.7 Introduction of ferromagnetic indicators

Crazing allows combining dyeing with incorporating any modifying additives to give additional useful properties to fiber (ferromagnetism, capability to absorb radiation, etc.) This gives broad possibilities to further improving technology of modifying fibers, in particular, to dyeing fibers in areas alternating with undyed ones and appears to be the most prospective way for obtaining fibers by realizing various mechanisms of protection of securities.

Similar to dyeing, the degree of the papers protection with metalized fibers can be enhanced by applying the metal to local areas of the fiber alternating them with "clean" areas. Patent [25] protects the technology of metal (Al, Sn, Ag, Co-Ni alloy) coatings deposition onto the fibers which are provided with discontinuous "mask" in the form of circular layers or layers in another form of water-soluble substance. After metal deposition, the "mask" is dissolved in water. Once this is done, the fiber has areas of metallic coating of the given form alternating with uncovered areas. Unlike the fibers processed by the crazing technology, such fibers quickly lose the metal layer in the case of mechanical damages.

The fibers were subjected to stretching in the colloidal solution containing nickel particles (particle size not exceeding 1 mcm) in the surface-active liquid carrier. Appearance of a bundle of PET fibers which are discontinuously modified with the colloidal solution by the mechanism of crazing is shown in Fig. 6.10. The fiber areas containing ferromagnetic particles have a characteristic gray-blue color which is in sharp contrast to the adjacent colorless areas.

Cryogenic (Great Britain), a high-field measuring installation, was used for registration of the fibers' magnetic properties. The fibers were placed into a cylindrical container (volume—0.1 cm^3) made of fluoroplastic. The measurements were taken by the induction method according to the imbalance scheme at frequency of 333 Hz

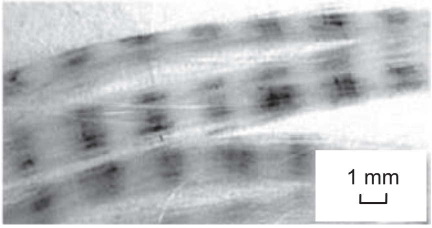

Fig. 6.10 The fibers which have been discontinuously modified with the ferromagnetic colloidal solution.

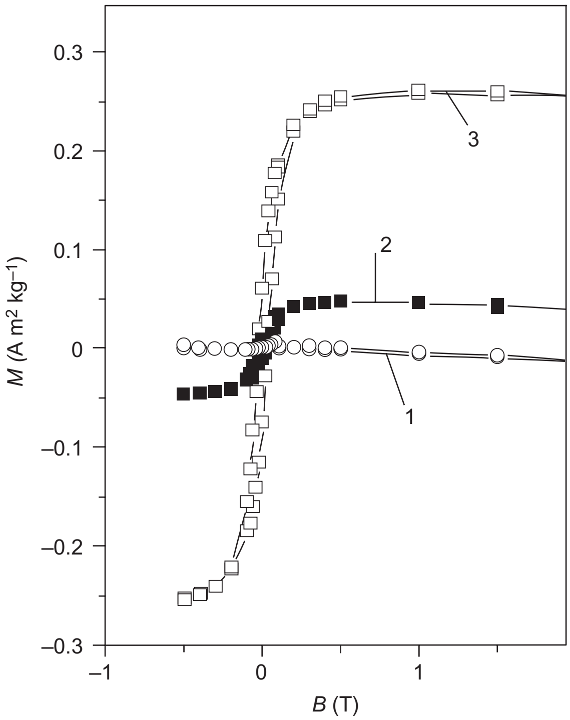

Fig. 6.11 Specific magnetic moment (M) of the fibers modified with nickel by the mechanism of crazing vs. the magnetic field induction (B): 1—initial fibers, 2 and 3—modified ones at draw ration $\varepsilon^* = 2$ and 3, respectively.

at room temperature in magnetic fields with induction of ±5T. Fig. 6.11 shows the dependencies of specific magnetic moments of the initial and modified PET fibers on the external magnetic field induction.

It can be seen that magnetization of the fibers modified with nickel at minimum draw ratio ($\varepsilon^* = 2$) enabling the initiation of crazes at the fibers' contact with the colloidal solution under study (curve 2) is considerably lower compared to the one at draw ratio, which is 1.5 times higher (curve 3). It is natural since deeper and intensive crazes formation is accompanied with the capture of larger quantities of particles of ferromagnetic filler. Initial PET fiber (curve 1) is not magnetized ($M = 0$) and does not react to the change in magnetic field.

The possibility of formation of polyester fibers with the defined distribution of magnetization allows the implementation of rather sophisticated systems for protection of securities meeting the requirements of modern cryptographic engineering [26].

When sealed in crazes of fiber, microinclusions of target additives do not undergo the effect of alkaline paper pulp which "extinguishes" luminescence and impairs other properties of modifiers introduced into the fibers. Metered-dose introduction of additives at local areas of the fiber is an optimal selection to meet the criteria of protection against counterfeit of the cellulose base of securities.

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Novel crazing technology applications

7

7.1 Radioabsorbing fibers

The abnormally high level of technogenic electromagnetic radiation (EMR) in the atmosphere due to rapid development of industrial production, intensive growth in the capacities of radio- and telecommunication services, the mass use of computers, cell phones, and microwave equipment has become a global problem of the 21st century. The increased levels of electromagnetic fields in the human environment have adverse effects on health of human beings and metabolism of biological environment [1], complicate operation of electronically controlled technological equipment [2], aggravate problems of information security and electromagnetic compatibility of radio electronic components [3]. Many of these problems could be solved by the textiles made of radioabsorbing fibers.

An overview of the methods for producing the polymer radioabsorbing materials (RAMs) shows that the basic technology of imparting the radiotransparent polymers with the capability to absorb EMR energy consists in filling the binders with current-conducting and magnetodielectric (ferrites, amorphous metals) powders and reinforcing with carbon and metallic fibers and fabrics [2–5].

Most often, RAM working in a wide range of EMR frequencies represent multilayer structures. Gradient RAM consisting of layers with different electromagnetic characteristics which arrangement ensures the increase in electric and magnetic losses of EMR energy as the radiation penetrates into the material are the most effective. Polymers filled with magneto-dielectrics are another type of wide-range RAM. EMR energy is transformed in them into the thermal one due to induction of eddy currents, dielectric and magnetic losses. Alternation of the layers which reflect and absorb the radiation yields a positive effect [4,5].

A wide group of plastics capable to absorb EMR energy has a structure of polymer composites filled and/or reinforced by technical carbon, carbon, and graphitized fibers in different textile forms—threads, bundles, bands, and fabrics [1,6].

Protective clothes and masking canvasses are made of machine-knitted fabrics with interweaving metal microwires or textile threads wrapped with microwires [7]. Such fabrics absorb EMR in the narrow band of radio frequencies due to reflection of the electric component of radiation [8].

Synthetic fibers are metallized by chemical reduction of metal ions in aqueous solutions to impart capability of absorbing EMR energy. During such processing, the fibers are loosened and acquire electrical conductivity which is proportional to the amount of deposited metal [9]. For the same reason, metal coatings are applied on the face of knitted fabrics using the vacuum deposition technique. Fabric covered with

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nickel has low coefficient of EMR energy absorption at low frequencies which results in the decrease in overall shielding effectiveness [10].

The technology for producing new RAM composites based on polyethylene (PE) recycled into the products (nonwoven cloths) by the melt blowing techniques is developed in [11]. Soft-magnetic powdered manganese-zinc ferrite with particles less than 50 mcm in diameter is used. Shields made of such materials do not require additional reinforcement, since the fibers are being cohesively linked to each other at the hardening of the thermoplastic binder.

At its core, the technology envisages the adjustable formation of the structure of the material which absorbs energy in the microwave band at two levels. The first level is the fibrous structure of the nonwoven cloth obtained by the melt-blowing technology [12]. The second one is the adjustment of the content of fibers with high-magnetic permeability in the fibers. Nonwoven fibrous cloth has a branched porous structure. It increases active surface scattering; in addition, it facilitates penetration of the electromagnetic wave deep into the cloth and considerable absorption of its energy due to electromagnetic losses caused by availability of the ferromagnetic filler.

Optimum thickness of a sheet fibrous shield which assures the highest radiophysical characteristics in the frequency range from 8 to17 GHz at relatively low consumption of materials and satisfactory physical and mechanical parameters is $h = 9–11$ mm [13]. The degree of the fibers filling (35%–40% by mass) with ferrite dispersity $d < 50$ mcm assures minimum value of the reflection coefficient (up to 30%) and maximum attenuation (to 5 dB) of EMR energy. The produced shields in the form of fibrous cloths with gradient of the ferrite filler concentration along the thickness of the shield are characterized by the increased efficiency of radio absorption (10–15 dB) in the microwave band (2–27 GHz) [14,15].

Electric and structural characteristics of the composite nonwoven RAM formed on the base of melt-blowing technology are estimated using a mix of physical and physicochemical methods of research. The engineered shields have a developed porous structure that increases the area of active surface scattering and facilitates penetration of EMR into the shield. Certain absorption of EMR energy occurs by the mechanism of magnetic losses due to availability of ferrite filler particles encapsulated in the binder which has the technology-specific fibrillar structure inside the fibers. Scattering parameters are increased owing to the large area of interphase boundaries and opportunity to give diverse forms to melt-blown shields, for example, in the form of truncated pyramids placed on the flat sheet base [16,17].

The fibers that are volumetrically filled with the radio absorbing substances are more expensive, firstly, because of a shortage of such substances and, secondly, due to the complexity of the manufacturing technology which includes additional operation to produce a semifinished product in the form of the polymer-filled granulate [18].

Prospects for using the radio absorbing textile materials depend on resolution of two conflicting requirements: sufficient radio absorbing efficiency and preservation of consumer properties of the textiles. In other words, imparting the fibers with the capacity to absorb the energy of radiation should not strongly influence their stress-strain characteristics and reliability of active particles fixing on the fibers. For that matter, the technology of the fibers modification with radio absorbing nano- and microparticles by the mechanism of crazing appears attractive.

We have developed the crazing technology to form experimental specimens of the radioabsorbing fibers which is as follows [19]. Polyethylene terephthalate (PET) fibers with nominal linear density of 0.33 tex are subjected to orientational drawing ($\varepsilon^* = 2.1$) in the surface-active liquid containing colloidal particles of amorphous soft magnetic material Fe/Ni/B.

The procedure for preparing a modifying liquid included the following operations: (1) preparation of the mix of $FeCl_3$ and $NiCl_3$ aqueous solutions; (2) addition (into the mix) of a certain amount of $NaBH_4$ which provides for complete reduction of Ni and Fe salts and formation of colloidal solution of the amorphous material Fe/Ni/B having nonstoichiometric composition; (3) separation of the colloidal solution disperse phase by centrifuging; (4) dilution of the obtained sediment with butyl alcohol; and (5) homogenization of the mixed product to the state of stable colloidal solution by using an ultrasonic disperser.

To detect the magnetic properties of Fe/Ni/B particles, a drop of colloidal solution was placed on the specimen glass of the optical microscope and then it was diluted with a drop of ethyl alcohol. Brownian motion of particles was observed at 40× magnification. When a permanent magnet (maximum magnetic induction B_r equaled to 16 mT) was brought to the drop, Brownian motion changed the directed movement of colloidal particles toward the magnetic pole. This is a direct confirmation of ferromagnetism of the particles available in the modifying solution.

Radiophysical characteristics of the modified fibers were assessed using a standing wave ratio (SWR) and attenuation of radiation energy of R2-61 (Fig. 7.1). The

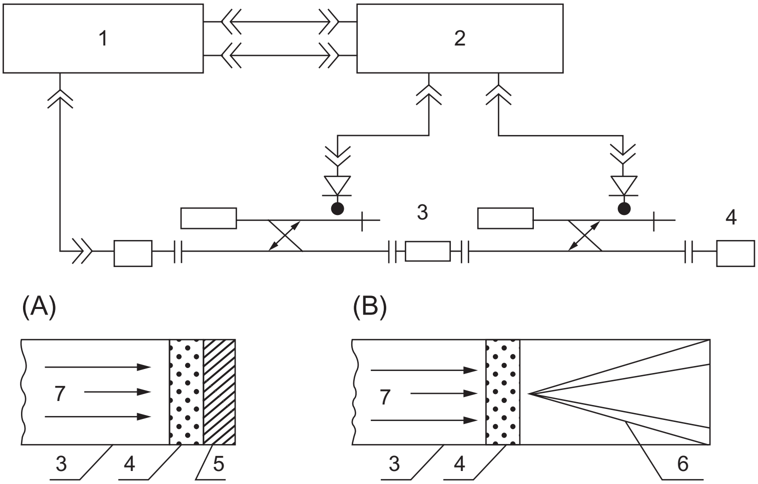

Fig. 7.1 Scheme of installation for SWR measurement and EMR attenuation with a short circuiter (A) and matched load (B): 1—microwave generator, 2—SWR measuring device, 3—waveguide duct, 4—specimen being studied, 5—short circuiter, 6—matched load, 7—microwave radiation.

reflection coefficient R and attenuation S of the energy in the microwave band 8.0–12.0 GHz were registered by reflectometry. A bundle of fibers was inserted into a cell made of radiotransparent fluoroplastic and representing an element of waveguide duct. The fibers' bundle in the cell was shaped as 30-mm-thick flat plate that corresponds to the wavelength of radiation with 10 GHz frequency. The cell was mounted into the wave guide of the panoramic measuring device. The attenuation value R was determined by the following formula:

$$R(\%)=(\mathrm{SWR}-1)\times 100/(\mathrm{SWR}+1).$$

The R value changed insignificantly when the fibers were being modified. Attenuation of microwave radiation energy by the modified fibrous amounted to $S=1.5$–2.5 dB. This is a rather small quantity which is lower than expected since it is considered [20] that availability of the magnetic absorption component allows a considerable expansion of the spectral window and an increase in EMR attenuation. In the radioabsorbing cloth, PET fabrics are used in the mix with cotton or wool yarn. It is obvious that the EMR-shielding ability of such fabric is insignificant. It seemed that the crazing technology was not suitable to form the fibers with a high S value to be used in protective clothing. However, an improvement in the technology which provided for introduction of radioabsorbing substance in small concentration into the fiber's structure may result in a significantly stronger shielding effect.

We have developed a technique to produce radioabsorbing fibers made of PET which consists in extraction of fibers in contact with the surface-active colloidal solution, their thermal stabilization and drying. The fibers are drawn in aqueous-alcoholic (3:2 by volume) saturated solution of seignette salt (SS) ($KNaC_4H_4O_6{\cdot}4H_2O$, potassium sodium tartrate tetrahydrate) at draw ratio $\varepsilon=2.1$–2.3 [21].

Ethyl alcohol is a strong surface-active agent for PET. Crazes are formed in the fibers at extraction in SS aqueous alcoholic solution. The solution "is drawn into" the opening crazes. Then, in the process of thermostabilization and drying of the fibers, the aqueous-alcoholic phase of the solution evaporates and SS microcrystals are settled in the crazes. They stay for a long time in the crazes even when the textiles are subjected to washing.

SS is a typical ferroelectric material, i.e., dielectric with spontaneous polarization properties which are heavily dependent on external influences. When the fabric made of fibers containing the SS microcrystals in the crazes is exposed to an EMR field, re-polarization of microcrystals occurs. EMR energy is consumed to change the polarization vector resulting in the radioabsorption effect.

As discussed in Chapter 2, it is necessary to draw the fibers up to the value $\varepsilon^*\sim 2.5$–3.0 to introduce colloidal (less than 1 mcm) particles into the crazes [22]. Viscosity of the SS solution is close to viscosity of water, and nanodimensional hydrates in the solution are considerably smaller than colloidal particles. As a result, the intensive "capturing" of the solution by the crazes occurs at lesser draw ratios of the fibers ($\varepsilon^*=2.1$–2.3). This allows a reduction in power consumption and a simplification of the drawing process. The obtained values of EMR attenuation for the bundle of such fibers were $S=1.5$–2.0 dB at the water-alcohol ratio of 3:2 in aqueous alcoholic solution of SS. In this case, the cost of the SS modifying solution is cheaper (by an order and a half of magnitude) compared to the surface-active colloidal solution of silver.

In principle, the problem of protection against EMR can be solved by using artificial leather (AL), i.e., the textile fabrics with polymer coatings. The latter are formed from melts, solutions, dispersions, plastisols based on polyvinyl chloride, polyolefins, polyamides, polyurethanes, etc. [23]. Sophisticated methods for application of polymer coatings onto the textile base aimed at improvement of stress-strain characteristics, an increase in fire-resistant properties, and maintaining AL performance efficiency at subzero temperatures are developed.

However, radiotransparent polymer coatings applied to AL can weaken EMR energy only when filled with radioabsorbing substances—metals, ferrites, ferroelectric material, etc.—which results in increased AL costs. This problem can be solved by introduction of water (which is a highly effective radioabsorbing substance) into the coating composition [24]. Water soluble polymers, for example, polyvinyl alcohol (PVA), can be used as the polymer base for such coatings. Its macromolecules contain vinyl units with hydroxyl (−OH) groups. When moistened, PVA and dipole water molecules are joined by hydrogen bonding, and macromolecules are cross-linked in the points of contact by covalent and ionic bonding [25]. As a result, hydrogel, a colloidal system with aqueous disperse phase containing supramolecular PVA fragments which form a stable spatial network, is formed.

We have developed a method for AL production which envisages application of PVA aqueous solution onto the textile base and its processing by thermostating of the impregnated textile material within the temperature range from −1°C to −5°C until the solution is frozen with subsequent thawing of the solution without temperature control [26]. When PVA solution is cooled down to $T = -1°\text{C}$ to $-5°\text{C}$ (taking into account possible supercooling), the solution aqueous phase turns into ice. The growing crystals of ice consolidate the walls of hydrogel polymer matrix in which new coordination-ionic bonds are formed and noncovalent cross-linking of macromolecules occurs. PVA hydrogel turns into the so-called cryogel [27]. This transformation is accompanied with the hydrogel shrinkage which causes displacement of the supercooled unbound water from the matrix. Cryogel acquires the increased (compared to the hydrogel) melting temperature ($T_m = 60\text{–}80°\text{C}$), tensile strength ($\sigma_t \approx 70\,\text{MPa}$) and elasticity ($\varepsilon \approx 25\%$), the rate of unbound water evaporation from it decreases ($w < 5\,\text{mg/cm}^2\,\text{day}$). Cryogel-based AL loses (without drying) stickiness which is typical for hydrogels, but retains flexibility inherent to the textile base, as well as radio absorbing ability (inherent to hydrogels) at $T > 0°\text{C}$ ($S = 10\text{–}12\,\text{dB}$) which remains practically unchanged for cryogel even at $T < 0°\text{C}$.

The material formed by the proposed method demonstrates the radio absorbing ability both at positive and subzero temperatures. The latter is quite unexpected since water becomes radiotransparent when turned into ice. Therefore, water in the cryogel coating structure is mainly in the bound state and does not freeze, acting as a radioabsorbing substance even at subzero temperatures.

The textile cloth produced by method [28] possesses even higher radioabsorbing properties. A layer of PVA aqueous solution in which SS is dissolved and which contains plasticizer (glycerin) is applied onto the textile cloth. The textile cloth with the layer of the modifying solution is thermostated at temperature from −1°C to −5°C until the aqueous solution of PVA is frozen, then the solution is subjected to thawing at ambient air temperature.

Mixing of PVA and SS aqueous solutions initiates diffusion of SS hydrates into the hydrogel polymer phase. Hydrates are immobilized in spatial network of macromolecules and are physically and chemically bonded with them. On freezing the mixed solution, the aqueous phase turns into ice. The ice microcrystals consolidate the walls of hydrogel polymer matrix in which new coordination-ionic bonds are formed in the cold and noncovalent cross-linking of macromolecules occurs. Hydrogel turns into a more stable cryogel in which the water is physically and chemically bonded with the macromolecules. During freezing-thawing and evaporation of the unbound water, SS microcrystals possessing the property of spontaneous electric polarization are settled in the free volume of cryogel polymer phase. The EMR influence on the coated textile fabric causes intensive polarization-depolarization of these microcrystals. It provides an additional mechanism to absorb EMR energy by PVA gel. In addition, hydrophilic SS crystals capture the unbound water from the cryogel, thus reducing its loss due to evaporation at operation of the radioabsorbing textiles. Attenuation of microwave radiation by such modified textile cloths reaches 14 dB.

The developed techniques can be applied at the enterprises which manufacture the textile-based flexible electromagnetic shields and fabric for EMR protective clothing.

7.2 Electroconductive fibers

The necessity to impart the synthetic fibers with electrical conductivity is caused, first of all, by stringent requirements to technical textiles in a number of industries. The second reason relates to static characteristics of fibers, i.e., with their ability to generate and accumulate static electric charge. When wearing clothes, as the fibers rub against each other, strong electrification may occur which reduces the consumer properties of textiles. Antistatic, i.e., slightly electrified, fibers allow the elimination of such a disadvantage.

Usual textile fibers in the initial state are dielectrics with specific conductivity of $\sigma < 10^{-8}$ Sm/m. Conductivity of antistatic fibers is 10^{-8}–10^{-2} Sm/m which is characteristic for semiconductors. Electroconductive fibers has $\sigma = 10^{-2}$–10^{6} Sm/m and higher. Synthetic fibers with the increased electrical conductivity are used to manufacture flat and rolled heaters, electromagnetic shields, antistatic fabrics, protective workwear, semiconductor paper, etc.

There are various methods to impart the synthetic fibers with electrical conductivity: surface metallization, carbonization, filling with metals, etc. [29]. This creates the possibility to make any chemical fiber electrically conductive. However, in view of technical and economic feasibility, the nomenclature of electroconductive synthetic fibers is rather limited [30].

Organic conductive fibers are made of polymers possessing semiconductor properties [31] or electroconductive polymers of the new generation [32].

The availability of the conjugated bonds (conjugation is the alternation of single and double bonds in the macromolecule structural formula) in the macromolecules of polymer semiconductors facilitates delocalization of electrons and an increase in their mobility. This phenomenon is pronounced in aromatic polymers—polyacetylene, polypyrrole, polyparaphenyl, etc. Conductivity is assured by transitions of electrons between various localized states of the macromolecule ("hopping" mechanism) or by electrons passing through a potential barrier (tunnel effect) [33]. The method of oxidative polymerization is used to synthesize a number of electroconductive polyconjugated polymers—polybiphenylene-ethylene, polybiphenylene-1,3-butadinylene, etc. [34].

Filling is the main method to produce electroconductive synthetic fibers. Dispersions of technical carbon and graphite, metal powders, etc. are used as fillers. To achieve specific conductivity of about 10^3 Sm/m it is necessary to introduce a filler (10%–50% by mass) into the fiber-forming polymer [29], which drastically changes the stress-strain characteristics of the fibers. Therefore, the main problem of forming the electroconductive filled fibers is the maximum preservation of elasticity and strength inherent to the initial fibers. The balance between the fibers' conductivity and deformability can be adjusted not only by the change in the filler concentration, but also by choosing fillers with optimal dispersion, configuration of particles and mechanism of conductivity between them, or by creating bicomponent fibers (BF) of the "conductive core-dielectric coating" type.

Processing with antistatic agents—SAS reducing the fibers' static electrification—is the method traditionally used in the textile materials processing technologies. Substances increasing the hydrophilic behavior and surface electrical conductivity of the fiber, reducing the friction coefficient, and changing the polarity of electrostatic charge on the fiber are used as antistatic preparations [35]. Application of 1% of cation-active SAS onto the surface of acetate fiber is equivalent to antistatic effect of introduction of this substance in the amount of 20% into the volume of fibers at their formation [36].

Fibers metallization is the application of metallic coatings on their surface. Synthetic fibers are metallized by gas-phase deposition, vacuum deposition, by means of electrophoresis, chemical reduction of metals from the salts solutions, electrochemical deposition, etc. [37]. An alternative method of metallization is the application (onto the fibers) of coatings made of electrically conductive varnishes containing finely dispersed (size ~1 mcm) powders of silver, copper, tin oxides, cadmium, indium, technical carbon, and graphite [38].

This short overview shows that there is an extensive technological basis for producing synthetic fibers with a broad range of electrical conductivity—from antistatic to conducting ones. The key question, however, is technical and economic feasibility of their production. From this standpoint, the technology of introduction of electroconductive nano- and microparticles into the fibers' structure by the mechanism of crazing is attractive.

The crazing technology to impart PET fibers with electrical conductivity is implemented through the use of the modifying colloidal solutions of copper and silver which are considered one of the best metal conductors. Three modifying compositions with copper, silver particles, and bimetallic silver/copper particles were used in experiments.

The colloidal copper solution was obtained from the base solution of copper acetate $Cu(CH_3COOH)_2{\cdot}H_2O$ in ethylene glycol with addition of aqueous solution of PVA. The latter performs the function of complexing compound for copper ions, stabilizer of the reduced copper, and surface-active component of the modifying composition. A solution of sodium hydroborate in ethanol is used as a copper reducing agent. Copper reduction occurs according to the following equation:

$$\mathrm{Cu}\left(\mathrm{CH_3COOH}\right)_2\mathrm{H_2O} + 2\mathrm{NaBH_4} + 6\mathrm{H_2O} = \mathrm{Cu} + 2\mathrm{H_3BO_3} + 2\mathrm{NaCH_3COOH} + 7\mathrm{H_2}.$$

Colloidal particles of copper are stabilized by “coats” constituted of PVA macromolecules. High viscosity provides for sufficient colloidal stability of the modifying composition.

Formulation and procedure of preparation of the silver-based compound are given in Section 3.5 and comply with the patent in Ref. [39].

Description of the formulation and technique for preparation of the composition based on colloidal solution of bimetallic silver/copper particles are given there as well and protected by the patent in [22].

PET fibers with linear density of 0.33 tex were processed by these compositions at the laboratory bench described in Fig. 2.14.

Electrical conductivity of the fibers was determined according to standard [40] which apply to elementary threads and bundles of synthetic fibers. Conductivity of the specimens was registered using a digital meter E7-8. The measurement diagram is shown in Fig. 7.2.

Measurements were taken as follows. The braided fibers’ bundle 1 was placed into clamps (3) and (4) which allowed the adjustment of the bundle tension using a screw pair. The bundle diameter was measured under tension and measuring electrodes (2) were connected to it. Conductivity G was measured in five areas along the bundle length. Specific cubic conductance σ_v was calculated by the following formula:

$$\sigma_v = \frac{Gl}{S}\left(\mathrm{Sm/m}\right), \tag{7.1}$$

where G is the measured value of conductivity, Sm; $l = 12$ mm is the distance between measuring electrodes; $S = \pi d^2/4$ is the cross-sectional area of the bundle of fibers, and d is the bundle diameter.

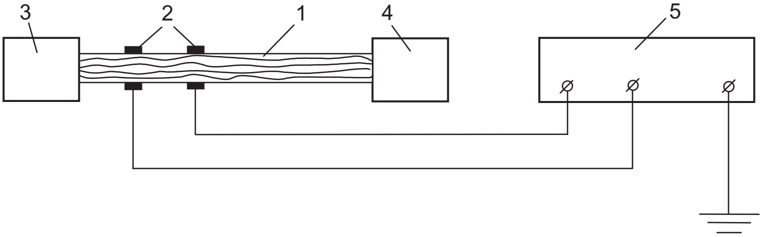

Fig. 7.2 Diagram for measuring conductivity of a bundle of fibers: 1—specimen; 2—measuring electrodes; 3, 4—clamps; 5—E7-8 measuring instrument.

Table 7.1 Conductivity of PET fibers of different types

Type of fiber	Diameter of bundle d (mm)	Average conductivity G (nSm)	Specific conductivity σ_v (Sm/m)
Initial	1.75	0.0274	1.26×10^{-7}
Cu modified	1.6	0.0252	1.36×10^{-7}
Ag modified	1.95	7.72	4.34×10^{-5}
Ag + Cu modified	1.05	98.9	1.37×10^{-3}

Table 7.1 shows the measured values of electrical conductivity for different types of specimens and the corresponding calculated values of specific cubic conductance.

Based on the data given in Table 7.1, the following conclusions can be drawn:

(1) PET fibers modification with copper nanoparticles by the crazing mechanism has produced practically no effect on the increase of the fibers conductivity, apparently, due to low concentration of copper in the modifying solution;
(2) processing with the silver-containing solution allowed to increase the fibers' electrical conductivity by almost two orders of magnitude (~10^{-5} Sm/m); and
(3) the maximum effect in increasing the electrical conductivity (by four orders of magnitude) was achieved at modification of the fibers with bimetallic silver/copper particles (~10^{-3} Sm/m).

Thus, specific cubic conductance of the initial PET fibers which have not been subjected to special cleaning from process liquids is about 10^{-7} Sm/m. By electrical conductivity, they can be related to "bad" (high-ohmic) semiconductors. Fibers modification by the mechanism of crazing creates the possibility to increase conductivity to 10^{-3} Sm/m. Such fibers do not fall into the category of electroconductive ones (of which the lower limit corresponds to 10^{-2} Sm/m), but they are good antistatic fibers which do not create a triboelectric charge. Bactericidal metals available in the fibers' structure provide them with additional antimicrobial activity.

7.3 Investigation of the possibility of bicomponent and superthin PET fibers modification

Satisfactory consumer properties of fabrics and knitted goods made of chemical fibers can be achieved if the fibers are imparted with waviness (nonlinearity, undulation of the fibers' longitudinal axis) imitating the appearance of natural fibers. Waviness is imparted to chemical fibers by texturing. The textured threads are voluminous, elastic, wear resistant, and possess high elastic stretchability and satisfactory hygienic properties [41].

The majority of the existing texturing techniques are based on mechanical deformation of thermoplastic threads and their heat setting in the stress state. As a result of deformation, the thread acquires helical, undulated or serrated waviness which is stabilized at thermal treatment.

The method for texturing the chemical threads by twisting, in particular, by the method of the so-called "false twisting," which allows the threads to be imparted with high straight and reverse twist in a single-stage process, is the most popular one. Textured threads obtained by the false twisting method are used mainly for production of knitted cloths and goods, including hosiery, and to a lesser extent for fabrics. The following is used to impart waviness to the threads made of thermoplastic polymers: crimping of threads by pressing in the chamber being heated (press-chamber technique), drawing of the thread along the steel plate edge, pneumotexturing [42].

Bicomponent fibers can be defined as "extruding two polymers from the same spinneret with both polymers contained within the same filament." A close relative is "co-spun fiber," which is a group of filaments of different polymers, but a single component per filament, spun from the same spinneret. The term "conjugate fibers" is often synonymous with bicomponent fiber, particularly in Asia [43].

Formation of bicomponent threads and fibers is a completely different method to impart the fibers with waviness. Fibers consisting of a core and coating are produced by the method of extrusion squeezing of the polymer melt through the extrusion nozzle. Bicomponent thread becomes wavy in the process of its orientational drawing and heat treatment. The tentative calculations shows that the costs of bicomponent thread production are 1.5–2 times lower than the costs for producing a classic textured thread [44].

By voluminous properties, the bicomponent threads are as good as mechanically textured ones, but unlike the latter they possess irreversible waviness which is consolidated by thermomoist processing. Along with high voluminosity, the BF have a number of unique technological properties.

The majority of BF are made of polyesters and their copolymers. The BF allow the combination of advantages of different polymers, i.e., "to design" a thread according to the assumed area of its application.

7.3.1 Structure, properties, and application areas of bicomponent and superthin chemical fibers

Bicomponent chemical fibers and threads are produced from melts (less frequently from solutions) of limitedly compatible or incompatible polymers or copolymers. Depending on the structure, BF of the following types are distinguished [44–46]:

- segmental (S/S)—polymer components are arranged in layers next to each other in the fiber's cross-section;
- core-coating (C/C)—polymer components are arranged "one around the other" in the fiber's cross-section; and
- matrix-fibrillar (M/F)—one or several polymer components, as an array of thin (<1 mcm) fibrils, are located in the matrix of another polymer component.

BF and threads are formed by using special extrusion nozzles. Due to the high viscosity of the matrix melt, the assigned arrangement of components is not disturbed in the process of BF production. Basic schemes of BF structure are presented in Fig. 7.3 and various structures in Fig. 7.4.

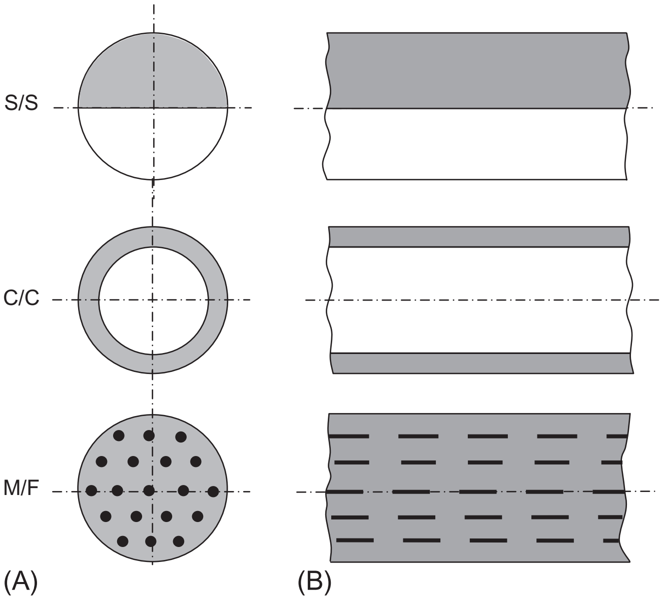

Fig. 7.3 Typical structures of bicomponent fibers in cross (A) and longitudinal (B) sections.

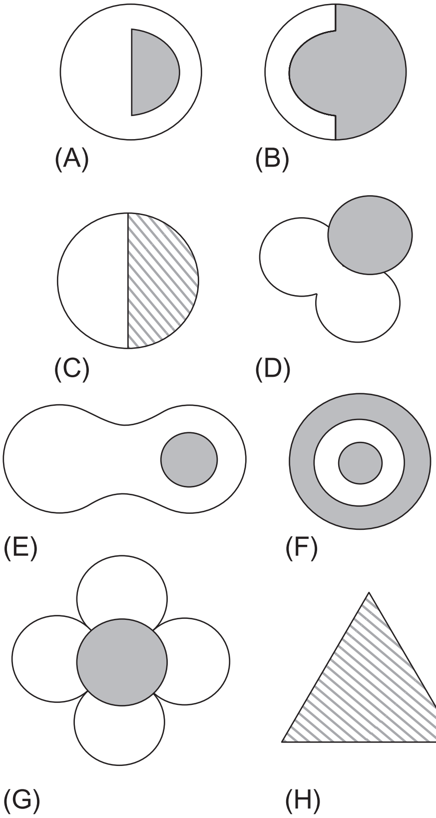

Fig. 7.4 Types of BF structures: (A, C) segmental; (B, D) intermediate between S/S and C/C; (E–G) core-coating; (H) matrix-fibrillar.

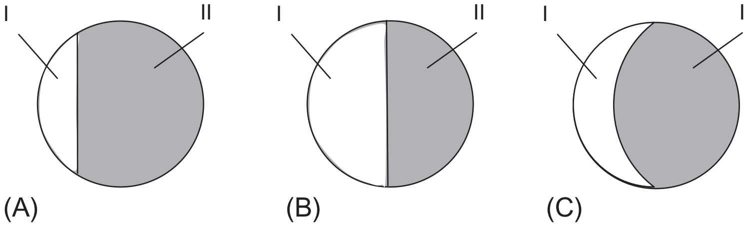

Fig. 7.5 Cross-sections of BF of segmental structure with straight (A, B) and crescent-like (C) lines which divide components I and II.

The degree of BF waviness depends on the form of its cross-section and distribution of the components in it. Fibers of the segmental structure with asymmetric arrangement of components have the greatest waviness. Waviness can be changed by the corresponding selection of components, their ratio in the fiber, and distribution of components across the fiber's cross-section, as shown in Fig. 7.5. Irrespective of the ratio of components, the waviness of Fig. 7.5B is considerably higher compared to Fig. 7.5A, and the waviness of Fig. 7.5C is several times lower compared to the one of Fig. 7.5B.

Bicomponent fibers and threads of segmental structure are used to produce textiles with high fiber waviness, wash and wear stability, size stability and elasticity, increased hygroscopicity, and durability. Such polymer fibers are close to wool in terms of their properties [47,48].

In BF of the *core-coating type* the high-shrinkage polymer is located in the central part of the fiber, while the ratio between the core share and the coating share by mass may change from 1:1 to 5:1. The use of fibers of such structure allows modification of only the coating material by imparting it with additional specific properties different from the ones of the core polymer material which determines the thread durability. Thus, it is possible to impart the fibers with better colorability [49], antistatic and dirt-resistant properties [50], resistance to wear, hygroscopicity, and smoothness [51].

BF of *matrix-fibrillar structure* are used as raw materials to produce nonwoven base of high-quality AL which properties are close to the natural one and considerably exceed the synthetic skin based on the usual fiber. In such fibers, the fibrils of one polymer are distributed in a certain way in the matrix of another. The fibers of such structure are formed using the immiscible polymers. As a rule, waviness of the fibers is insignificant and allows them to be used in the production of bulked threads. The matrix-fibrillar structure is convenient to obtain fibers with the increased electrical conductivity [52] and high strength [53].

Ultrathin (superthin) synthetic fibers (microfibers) are used for production of securities, synthetic paper, AL, nonwoven materials, reinforced fibers and films, and fine filters.

The microfibers are divided into micron (1–10 mcm dia) and submicron ones (<1 mcm). Several techniques to produce microfibers are developed [54]:

- blowing the polymer melt jets at the discharge from the extrusion nozzle with heated air flows;
- drawing the fibers with large drawing ratios;

Table 7.2 **Physical and mechanical characteristics of complex threads made of ultrathin and usual polyoxymethylene fibers**

Property indicators	Thread	
	Usual	Ultrathin fibers
Linear density (tex)	6.66	1.37
Diameter of elementary thread (mcm)	86.0	0.3
Density (kg/m^3)	1403	1428
Tensile strength (Pa)	0.78	1.08
Relative elongation at rupture (%)	14.4	14.4
Strength retention (%)		
In the node	15	77
In the loop	19	80

- forming by high-speed extrusion;
- fibrillation of the drawn high-oriented films; and
- releasing the microfibers from the fibers of the matrix-fibrillar structure by extraction of the matrix component with a solvent which is inert relative to the fiber-forming polymer.

Threads made of ultrathin fibers differ in softness, pleasant touch, and wool-likeness [55]. A comparison between properties of the usual thread and the thread made of ultrathin fibers is given in Table 7.2.

7.3.1.1 Application areas

In textile production, the bicomponent threads and fibers are used for production of knitted and woven products of wool-like and cotton-like type, silk products, plush, velvet, artificial fur and suede, carpets, nonwoven materials, etc. Application of BF and threads in the special purpose products—electroconductive, light-conducting, ion exchange and hollow fibers—is of special interest [44].

Bicomponent threads are used as the basis to create textile materials with extremely opposite electrical properties: both electroconductive and electret—electrical-field sources. The electret textiles are used in engineering to manufacture electrostatic dust collectors, filter dust collector, etc. Bicomponent *fibers-electrets* usually have the "core-coating" structure. In the process of polarization, a high voltage is applied to the core. A metal wire or carbon fiber with electrical resistivity of less than $10^{10}\,\Omega\,\text{cm}$ is used as a rod component (core). The coating is usually made of PE or polyvinylidene fluoride with resistivity of not $<10^{14}\,\Omega\,\text{cm}$.

BF-based *electroconductive materials* have a core which is about 30% of the mass of the fiber. The core consists of a thermoplastic polymer (most often, polyether) filled with technical carbon which contains polyethylene glycol—the carbon particles disperser. The coating is made of polyamide-6. The resistivity of such fiber is $7\times10^4\,\Omega\,\text{cm}$.

In addition, BF can be used for special purposes, such as production of *fire-retardant* materials. The coating of fire-resistant BF consists of polyether copolymer and a core of polyether with addition of 5%–40% of a fire-retardant agent, for example, brominated diphenyl ether. Fire-resistant BF containing the fire-retardant agent as a part of the core have the advantage of high mechanical strength. It is higher than the fibers in which the fire-retardant agent is distributed evenly.

BF of the “core-coating” type are used in the modern *fiber-optic communication* systems instead of glass and quartz bicomponent threads. Specific requirements to the materials suitable for producing light-conducting fibers considerably constrict the nomenclature of polymers that can be used for this purpose. Usually, a light-conducting core with high transparency consists of polyacryl methacrylate with the index of refraction of 1.48–1.51. To achieve a signal with the increased light intensity, the index of refraction of the coating shall not exceed 1.45. Polysiloxanes are usually used as the coating material.

BF of the “core-coating” structure are used at production of nonwoven cloths as conglutinating (interfusing) elements. At its core, the technology of their formation envisages the following. Nonwoven fabric is composed of usual chemical fibers and BF which content in the material does not exceed 2%. BF are formed from polymers which melting temperatures shall not differ for more than 20 degrees. In the process of obtaining the material, the fibers are heated to the melting temperature of low-melting coating, as a result of which we observe welding of the nonwoven cloth at points of contact with BF. Production of BF of “core-coating” structure is organized at JSC Mogilevkhimvolokno, where a low-melting PET copolymer is used as the coating material.

Thus, BF and threads of various compositions and structures have a wide application both in the traditional area of knitted and woven products production, and in the industry of fibrous materials with special properties.

7.3.2 Modification of bicomponent polyester fibers

Newly formed bicomponent PET fibers manufactured by JSC Mogilevkhimvolokno with linear density of 0.44 tex (Belarus Engineering specification TU BY 700117487-2009) were used for laboratory studies. The BF structure represents a “core-coating” system. The coating is made of copolymer with a melting temperature of 115–135°C and amounts to 30% of the fiber’s mass. The core of polyether with $T_m = 260–262°C$ amounts to 70% of the mass. Durability of fibers is 460 g/tex; relative elongation is 62%.

BF were modified at the test bench imitating the technological process of drawing and temperature stabilization of fibers at the staple machine. The fibers’ draw ratio was regulated within the range $\varepsilon^* = 2.5–3$; the fibers were found to be torn at $\varepsilon^* > 3$. On bringing the fibers into contact with the modifying liquid, initiation of a neck occurred when the fiber was drawn.

Images of the cross-section of BF used in the experiment are presented in Fig. 7.6. To produce the specimens, a bundle of fibers was encapsulated in epoxy resin and, after curing of the latter, was cut with a blade normally to the direction of the fibers. Diameter of the initial fiber $d \approx 40$ mcm, coating thickness $h = 3–4$ mcm were measured with a scanning electron microscope (SEM) VEGA//TESCAN with the software installed.

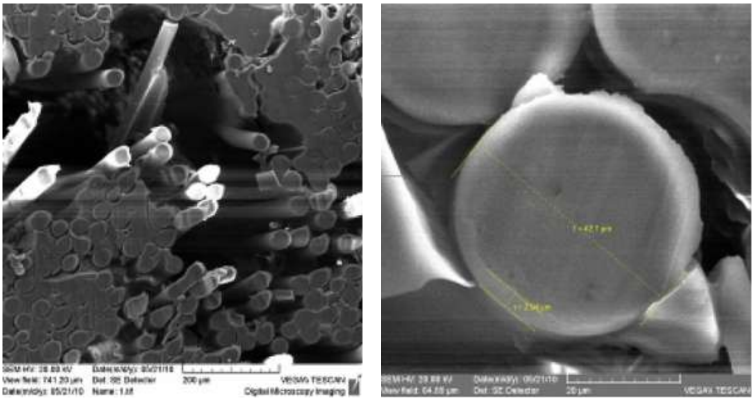
(A) (B)

Fig. 7.6 End faces of bicomponent fibers at different magnifications: ×100 (A), ×1000 (B).

Changes occurring in the structure of bicomponent PET fibers in the course of their orientational drawing were registered to determine the possibility of their modification by the mechanism of crazing. Orientational drawing of the elementary fiber was carried out using a device, of which the scheme and general view are presented in Fig. 2.3.

Elementary BF (in the form of a loop) were fixed on racks (3). Then the device was placed under the lens of optical microscope and the rack-fixing plates were moved apart by handle (5). It allows the moment of neck formation on which cracks are initiated to be registered. SEM images of BF subjected to orientational drawing in air are presented in Fig. 7.7.

The structure of BF subjected to orientation drawing in the adsorption-active environment (70% aqueous alcoholic solution) was studied according to the same scheme. The moment of the neck initiation was registered with the optical microscope. Then, after evaporation of the solution, the fiber surface was studied with SEM. SEM images of BF subjected to orientational drawing in alcohol solution are presented in Fig. 7.8.

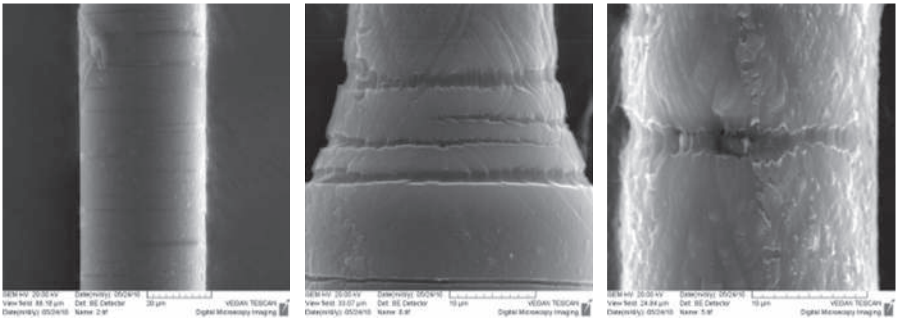
(A) (B) (C)

Fig. 7.7 Bicomponent fiber subjected to orientational drawing in air: (A) area of the fiber area in the prestressed state; (B) area of the neck initiation; (C) area of the drawn BF.

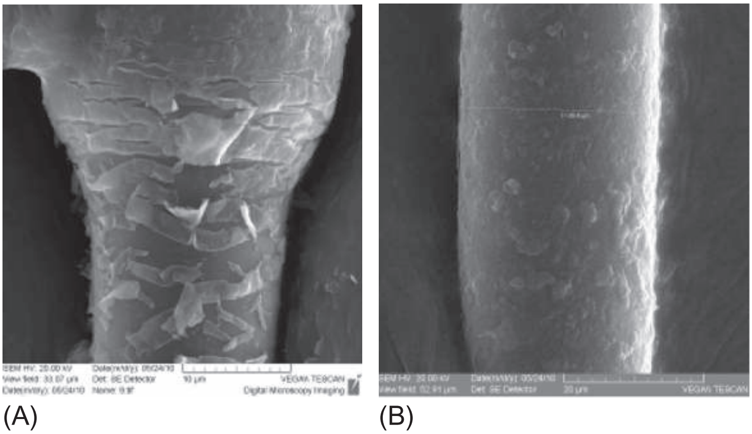

Fig. 7.8 Bicomponent fibers subjected to drawing in alcohol solution: (A) area of the neck initiation and (B) the drawn area of the fiber.

The following conclusions can be made based on analysis of images of the fibers subjected to orientational drawing in air presented in Fig. 7.7:

(1) surface of the initial fiber (Fig. 7.7A) is smooth, without visible flaws and defects;
(2) at fiber drawing, a neck is formed in the area of which ring cracks (Fig. 7.7B) are initiated, apparently, as a result of the coating rupture; and
(3) the surface of the drawn fiber (Fig. 7.7C) has a flake structure, while the flakes are absent in the places of cracks initiation.

Thus, BF orientational drawing in air results in discontinuities in coating and formation of highly developed flake structure on the fiber surface.

As can be seen in Fig. 7.8, patterns of BF drawing in the alcohol solution environment are somewhat different:

(1) neck initiation is accompanied with the coating fragmentation into individual irregularly shaped "patches" that are 3–5 mcm in size (Fig. 7.8A);
(2) the drawn fiber consists of the core on which surface the coating fragments are located (Fig. 7.8B); and
(3) formation of the crazes on the BF core is not observed.

Microbiological testing of BF subjected to modification with the triclosan-based antimicrobial composition was carried out with respect to pathogenic bacteria *Staphylococcus aureas*. It turned out that the fibers possessing antimicrobial activity before washings (a zone of suppression of growth of microorganism is 5–7 mm) lose their protective properties after 3–5 cycles of heat and wet processing. It is obvious since the crazing process is localized in the coating which breaks down and has practically no effect on antimicrobial activity of the fibers. As a result, the fibers do not demonstrate a long-lasting bactericidal effect.

7.3.3 Experiments on producing superthin polyester fibers

Newly formed PET fibers manufactured by JSC Mogilevkhimvolokno with linear density of less than 0.12 tex were used for laboratory studies. Diameter of the initial

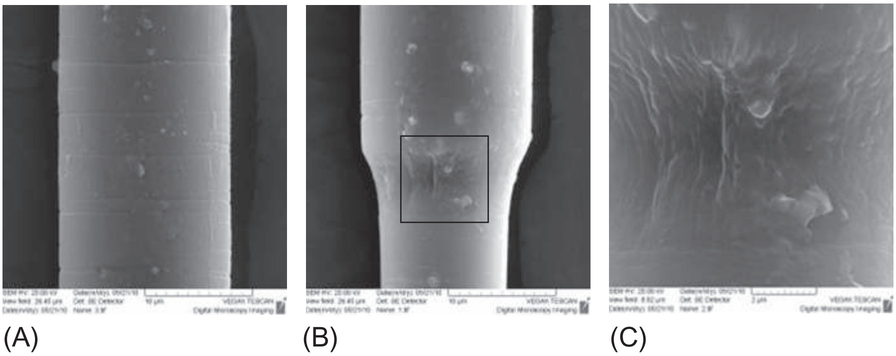

Fig. 7.9 Fibers subjected to orientational drawing in 70% alcohol solution: (A) area of the fiber area in the prestressed state; (B) area of the neck initiation; (C) distinguished area of the neck in (B).

fiber $d \approx 15$–17 mcm was measured with a SEM VEGA//TESCAN with the software installed. Changes occurring in the structure of the fibers in the course of their orientational drawing were studied according to the scheme described in the previous section.

The fibers are evenly drawn in air without a noticeable change in the surface structure in the area of the neck initiation.

As can be seen in Fig. 7.9, the structure of the fiber subjected to orientational drawing up to $\varepsilon^* \approx 3$ in the surface-active environment does not contain areas of the crazes initiation and spreading, which clearly shows that this method cannot be used for producing superthin fibers. A rough surface with formation of microroughnesses of 1–2 mcm high is formed in the neck area.

We made an attempt to enhance the microcrazing effect in elementary PET fibers by the corona discharge treatment. It was assumed that the influence of the corona would result in the activation of the fibers' surface and, probably, break down into fibrillar formations.

Specimens of the elementary polyester fibers were fixed on the device shown in Fig. 2.3. The device with specimens was placed in the zone of impact of the corona discharge of positive and negative polarity. In both modes, the discharge voltage was $U = 8$–10 kV, exposure time $t = 30$ min, distance from the corona electrode to the specimen $h = 50$ mm.

Digital images of the fibers processed in the positive corona are given in Fig. 7.10. Drawing in air up to $\varepsilon^* \approx 3$ results in no visible changes in the fiber structure. Drawing in the surface-active liquid (Fig. 7.10A and B) is accompanied with formation of plate-like fragments (1–2 mcm in size) on the surface of the fibers. Apparently, the impact of tensile stresses on the fiber's surface activated by the corona discharge results in the breaking of intermolecular bonds and the formation of the detached-from-the-fibers fragments which are held on the fiber surface by the adsorption forces.

Similar results are obtained when processing the fibers in negative corona; SEM images of the results are presented in Fig. 7.11. On drawing in the alcohol solution (Fig. 7.11A and B), irregularly shaped fragments with the size in micrometer units are formed on the fiber surface (similar to positive corona).

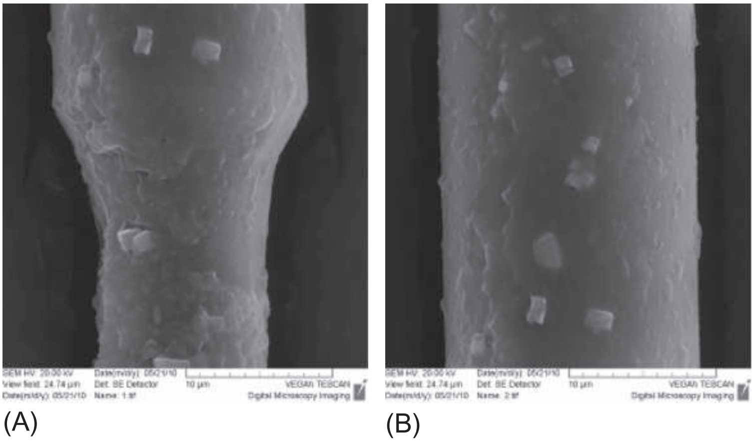

Fig. 7.10 PET fibers subjected to processing with the positive corona, with subsequent orientational drawing in 70% alcohol solution: (A) area of the neck initiation and (B) area of the drawn fiber.

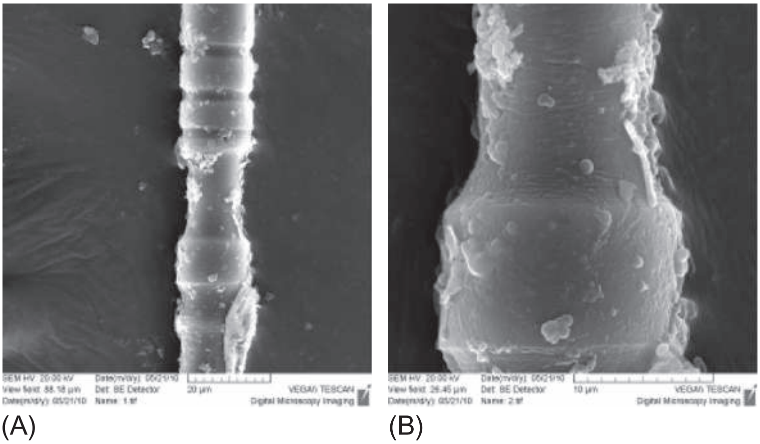

Fig. 7.11 PET fibers subjected to processing with the negative corona and subsequent orientational drawing in 70% alcohol solution. Magnification: ×800 (A), ×2000 (B).

Thus, the crazes formation of PETF-fibers at drawing in the surface-active liquids up to $\varepsilon^* \leq 3$ does not facilitate the breakdown of the fibers into superthin fragments. As we have shown previously, the fibers with linear density of 0.33 and 0.17 tex are subjected to intensive crazing. According to the results of experiments, one can see that fibers with linear density of 0.12 tex are not subjected to crazing, i.e., the threshold thickness of the crazes formation ($\varepsilon^* \leq 3$) corresponds to the range of 0.12–0.17 tex. This can be explained by the different degree of crystallinity of fibers: as a rule, it is significantly lower for thin fibers compared to the fibers with larger values of linear density.

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Conclusion

Analysis of the essential features characterizing the structural and charge state of polymers subjected to crazing has led to the conclusion that crazing corresponds to the category "physical phenomena." As a result of crazing, polymer exists in a special form, of which the distinctive features are: (1) availability of fibrillar formations in the initial crystalline-amorphous structure; (2) irreversibility of the fibrillization process; and (3) the possibility to develop this structural state only towards reduction of intermolecular interactions that, in the limiting case, will determine phase transformation of the initial structure into the state of collectively oriented macromolecules. Deformation of a polymer specimen prior to initiation of shear bands in the surface-active environment is a necessary and sufficient condition of crazing initiation.

Crazing significantly expands technological possibilities for polymer modification with any substances, including those that are thermodynamically incompatible with them. A remarkable advantage of the crazing technology is as follows. Adsorption of the modifier on the newly formed (in the process of crazing) surfaces and "closing" of crazes after the load is relieved provide for sealing of the substance available in the craze and possibility of its long (years) release to the surface of the polymer matrix.

The application of crazing in technologies for synthetic fibers processing has allowed fibers to be imparted a number of properties unattainable by traditional methods of processing. It is natural that engineering companies strove to make new technologies inaccessible to competitors. This has become an obstacle to exchange of information and generalization of results of crazing technologies; in addition, it has practically stopped the search for new areas of their effective application at polymer processing. In this book we have tried to overcome that obstacle and to define the limits of areas of reasonable use of crazing in the totality of synthetic fibers technologies. This became possible owing to development of this theme within the framework of scientific and technical program "Composite" of the Union State of Russia and Belarus and to the creative cooperation between specialists of MPRI of NAS of Belarus in physics, mechanics, and technology of polymer processing and specialists of the Central Research Institute of Complex Automation of Light Industry (JSC TSNIILKA, Moscow) in the field of textile materials science and technology.

As a result, the following pilot and experimental-industrial batches of polyester fibers were produced and subjected to standard test methods: biostatic and biocidal fibers modified by silver and triclosan; odorized fibers (with smell of lavender); fibers of reduced combustibility modified by fire-retardant agents; pyrethroid-containing repellent fibers; and antistatic fibers modified by colloidal solutions of silver and copper. The developed technological processes are adapted to the industrial technologies for synthetic fibers production. Production of industrial batches of the targeted modified fibers and their approbation in new types of textiles provided for evaluation of consumer properties of the products with special properties, the capacity of the market for such products, and its competitiveness as compared to similar products, primarily those produced in China.

In conclusion, it should be noted that possibilities of the crazing technology at processing the polymer materials are far from exhausted. Therefore, the researches aimed at the use of crazing at creation of electret and piezoelectric polymeric dielectrics, polymer-polymer nanostructured blends, etc. are intensively developing in recent years. This allows us to look with optimism at the perspectives of crazing technology development in different industries.

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