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PREPARING OF WOOL FIBERS FOR THE PRODUCTION OF HIGH-QUALITY FABRICS AND KNITWEAR

Monograph

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The monograph is devoted to the development of scientific fundamentals of the modification of coarse wool fiber using electrical-discharge nonlinear bulk cavitation. It is shown that the use of this innovative cost-effective and environmentally friendly method in the preparing of coarse wool fiber, including pigmented wool fiber, will allow the use of this raw material for the production of high-quality textile materials and knitwear.

The monograph presents the scientific substantiation of the use of electrical-discharge nonlinear bulk cavitation as a method of preliminary modification of coarse wool fiber in the process of its bleaching, as well as a possible mechanism of the modification of wool fibers, due to the complex influence of processes occurring during the electrical-discharge treatment in the working medium. As a result of the comprehensive studies of the physico-mechanical, technological and chemical properties of bleached wool, the advantages of using preliminary electrical-discharge treatment in the process of wool bleaching have been proved experimentally, which consist in increasing the resistance to hydrolysis, to action of oxidants and reducing agents of bleached wool, as well as in reducing the felting and slight decreasing in the fineness of the fiber.

The monograph is of scientific and practical interest for scientists and specialists in finishing production, lecturers, graduate students and students studying the chemical technology of fibrous materials.

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INTRODUCTION

In recent years, there has been an increase in the world consumption of wool fiber, which due to the unique complex of natural properties is a valuable raw material for the production of a wide range of textile materials. Analysis of the wool goods market shows that the main demand for wool fiber is provided by wool clothing [1]. The second largest branch of wool products is the production of carpets and floor coverings.

However, today Ukrainian wool products occupy an insignificant part of the market [2]. The decrease in production of wool materials is associated with a deficit of Ukrainian raw materials, along with the growth of foreign exchange costs for the purchase of wool raw materials abroad [3].

The main condition for reducing the dependence of the wool industry of Ukraine on imports is the sustainable development of its own raw materials base. To date, Ukrainian wool, a significant part of which is coarse, can not cover the needs of textile enterprises in Ukraine. The decline in wool production is associated with a decrease in the number of sheep and an increase in the share of low-grade raw materials coming from the private sector [4, 5]. The existing conditions put the wool branch of light industry in front of the need to improve the quality of products with the existing structure of the raw material base, which can be achieved by introducing new technologies that will ensure the production of competitive textile materials.

A promising way to increase the functionality and competitiveness of wool is the modification of the fiber, which allows manufacturers to give wool the necessary consumer properties [6]. In modern conditions it is economically expedient to develop combined methods for the modification of textile materials with the basic technological processes for their finishing.

In traditional finishing technologies, in particular bleaching, wool fiber undergoes significant damage to the protein structure, which leads to a reduction in its strength properties and increase in felting. This negatively affects the efficiency of further processing of bleached wool, as well as the quality of finished products. In this regard, the most practical interest is the modification methods, which ensure minimal damage to wool fibers in the process of bleaching.

Special attention is now paid to the use of physical influences, which include an electrical impulse discharge in a liquid, accompanied by the occurrence of electrical-discharge nonlinear bulk cavitation (EDNBC). Studies conducted in Ukraine and abroad showed the principle possibility of its use in various technological processes.

Thus, the development of technologies of wool fibers bleaching with the use of EDNBC in order to minimize its damage, improve the quality of finished products and reduce its cost is an urgent task.

The goal of the work was to develop technologies of wool fibers bleaching with the use of EDNBC in order to improve the quality and increase the competitiveness of the finished product by reducing its cost.

To accomplish the goal of the research, the following tasks have been set:

– to develop technologies of semi-fine wool and coarse pigmented wool bleaching with the use of electrical-discharge processing as a method of preliminary modification;

– theoretically substantiate and experimentally confirm the effectiveness of the use of preliminary electrical-discharge processing for the modification of wool fiber;

– to analyze and establish the influence of EDNBC on the surface properties of semi-fine and coarse wool, to determine the technological parameters for conducting the process of electrical-discharge processing.

SECTION 1

STRUCTURE OF WOOL FIBER AND ANALYSIS OF METHODS FOR ITS BLEACHING

1.1. Features of the structure and chemical composition of wool fiber

Sheep, camel, goat and rabbit wool as well as down and mohair are used as wool raw materials in the light industry. For the textile industry, the most important is sheep's wool, which is divided into species depending on the fineness: fine, semi-fine, medium and coarse [7, 8].

The fine wool consists mainly of thin, finely crimped down fibers, has a staple structure and is distinguished by high uniformity in fineness and length. The average fineness of fine wool varies within 14.5-25 μm, the average length is 40-70 mm. Fine wool with an average length of more than 55 mm goes to French system of spinning, and less than 55 mm goes to woolen condenser spinning.

Semi-fine wool consists of fibers of down or fine transitional hair. It is distinguished by its uniformity in fineness and length, has a staple structure and a larger crimp of the fibers than in fine wool. The average fineness of semi-fine wool is 27 μm. In terms of its technical properties, the semi-fine wool approaches a fine one and is intended mainly for the production of combed yarn [7, 9-13].

The medium wool is not uniform, it consists of down and transitional hair with a small admixture of fine ordinary hair and has a structure similar to braids. The homogeneous wool consisting of a fine ordinary hair and a transitional hair one can also refer to medium wool.

Coarse wool has a structure similar to braids and is not uniform mixed hair, as it is characterized by the presence of all types of wool fibers: fine down, transient hair, ordinary hair and brittle hair. The ratio of different types of fibers in the wool may be different depending on the breed and the sheep's in-breed characteristics, which determines the value of coarse wool.

Wool fiber is a horny formation of epidermal origin, consisting of a keratin protein.

The wool fibers have a heterogeneous histological structure. The fiber of fine wool consists of two layers, namely the outer scaly, or cuticle, and the inner cortical layer, namely the cortex. The coarser fiber also contains a core layer [7, 13-17].

The structure of a fine merino wool fiber is shown in Fig. 1.1 [11].

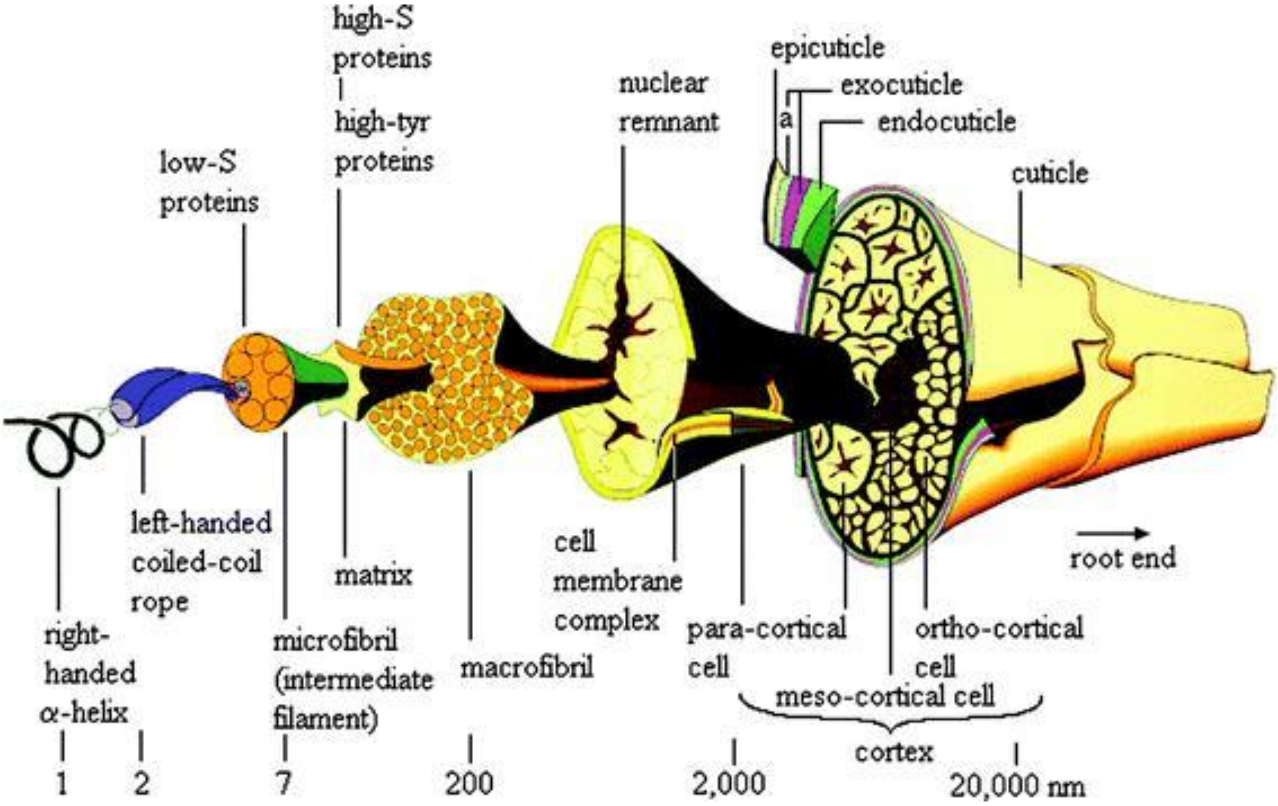


Fig. 1.1. Histological structure of wool fiber.

The fiber consists of scaly (cuticle) and cortical (cortex) layers and has a pronounced natural crimp due to the presence of ortho- and paracells in the cortex, the third core layer is present in coarse fibers. The presence of the core reduces the mechanical strength and elasticity of the fiber, but increases its heat-shielding properties and increases gloss.

The cuticle is the outer surface of the fiber, which protects it from mechanical, chemical and biological factors of influence, affects the wettability of the wool and its felting [18, 19]. In fine wool, the thickness of the scaly layer is the thickness of one cuticle cell, except when two scales overlap each other. The thickness of the cuticle of coarse fibers can reach 15 layers of scales [16]. The ability of the fiber to felt depends on the state of the cuticle scales, their integrity and the density of adhesion to each other [7, 10, 20, 21].

Cuticle cells consist of two main layers: exocuticle and endocuticle, differing in content of cystine, and surrounded by a thin protective membrane named epicuticle [8, 9, 13, 16]. The epicuticle, having a high resistance to the action of acids, oxidants, reducing agents, enzymes and to a certain extent alkalis, forms a diffusion barrier for the penetration of chemicals into the fiber.

To the inner side of the epicuticle adjoins a thicker layer named exocuticle, which is a protein with high hydrophobicity, high sulfur content and a high degree of cross-linking of polypeptide bonds, which causes its extreme resistance to the action of enzymes and chemical reagents.

The deepest layer adjacent to the cortex is the endocuticle. This is a hydrophilic layer with a low sulfur content, which consists of nonkeratinic cytoplasmic residues and pre-existing follicles, is soluble in acid and not resistant to enzymes [8, 18, 19].

The cortical layer (cortex) is under the cuticle, constitutes the bulk of the fiber and determines the basic physicomechanical and in many respects the chemical properties of the wool. It consists of spindle-shaped cells located in the direction of the length of the fiber, sufficiently tightly pressed against each other.

The spindle-shaped cells of the cortical layer consist of macrofibrils, which in turn consist of microfibrils with a diameter of about 0.05-0.2 μm of various lengths arranged by bundle and having an ordered crystalline structure, but mostly characterized by a disordered amorphous structure [13].

The voids separating the macrofibrils are filled with a cystine rich intermacrofibrillar substance.

Macrofibrils consist of microfibrils, which, in turn, are divided into protofibrils, which are spiral interlacings of two or three α-helical chains (amino acids). The fibrillar supramolecular structure of keratin is characterized by a high degree of orientation and crystallinity and immersed in the interfibrillar substance, a matrix similar in structure to keratin, but having an amorphous structure [10].

The cell membrane complex binds all cells of the cortex in a single system. It arises at the final stage of keratin formation of the wool between the membranes of cortex cells and the cuticle. This layer differs from living cell membranes with a low content of phospholipids and consists mainly of proteins, free fatty acids and waxes (cholesterol and desmosterol) [22].

The core layer is present in coarse wool fibers, in which the content of core cells reaches 15% [8]. The framework of the cells of the core layer consists of a protein similar to the microfibril protein of the cortical layer, but in the core layer the microfibrils are oriented along the transverse walls rather than along the fiber as in the cortical layer. Proteins of the core layer are characterized by a very low content of cystine and are relatively resistant to the action of a variety of chemical reagents, including caustic alkalis. The high chemoresistance and insolubility of the proteins of the core cells is explained by the presence of amide cross-linkages formed by the amino groups of lysine and the carboxyl groups of glutamine or aspartic residues of nearby peptide chains [11].

The amino acid composition of wool fibers is well studied, but it is noted that for the whole wool fiber and its histological elements it is significantly different [8-11].

By structure, keratin is a composite complex containing bundles of high-molecular chains interacting, both in the longitudinal and transverse directions. The main polypeptide chains of keratin are oriented along the fiber and are connected by a large number of cross bonds due to salt, covalent and hydrogen bonds, as well as Van der Waals' forces [8, 9].

The formation of salt bonds between the polypeptide chains in the keratin macromolecule is due to a significant content of the basic (arginine, histidine, lysine) and dicarboxylic amino acids (aspartic and glutamine).

The main covalent bond between the polypeptide chains is the disulfide (cystine) bond, which firmly bonds the polypeptide chains of keratin. Disulfide bond causes a number of specific chemical and physico-mechanical properties of the wool, for example, complete insolubility in water and organic solvents, special strength and high elasticity of the fibers [9]. Disulfide bonds can be modified, broken down or hardened and cause significant changes in the chemical and physico-mechanical properties of the fiber [11, 16].

Hydrogen bonds are formed between groups of peptide bonds –CO–NH– of neighboring polypeptide chains, and also due to a significant amount of hydroxyl-containing amino acids (serine and threonine).

The structure of the side chains largely determines the physico-chemical properties of proteins: the position of the isoelectric zone, the ability to solvate and hydrate. The active functional groups in the side chains mainly cause the chemical reactions characteristic of protein substances [8-11].

The natural coloring of wool fibers is given to the pigments located in the fiber cortex in the form of granules of ellipsoidal shape. Microscopic studies show that the pigment is mainly located in the interfibrillar substance, and the amount of colored granules increases from the center to the surface of the fiber [8]. Part of the pigment is located diffusely in the fiber. In the paracortex, its content is greater than in the orthocortex. A certain proportion of the pigment is found in the scaly layer.

The formation of the pigment occurs during the period of hair growth and is associated with partial hydrolysis of the resulting proteins to tyrosine, the oxidation of which in the presence of the tyrosinase enzyme and subsequent polycondensation leads to the formation of colored products named melanins [23, 24].

Depending on the sources of formation, melanins are divided into eumelanins and pheomelanins. The source of eumelanin formation is tyrosine, from which pigments containing C, H, N, and O are formed as a result. The sources of pheomelanins are tyrosine and cysteine, which turn into sulfur-containing pigments [25-27]. The stages of biosynthesis of melanins are schematically represented in Fig. 1.2 [28].

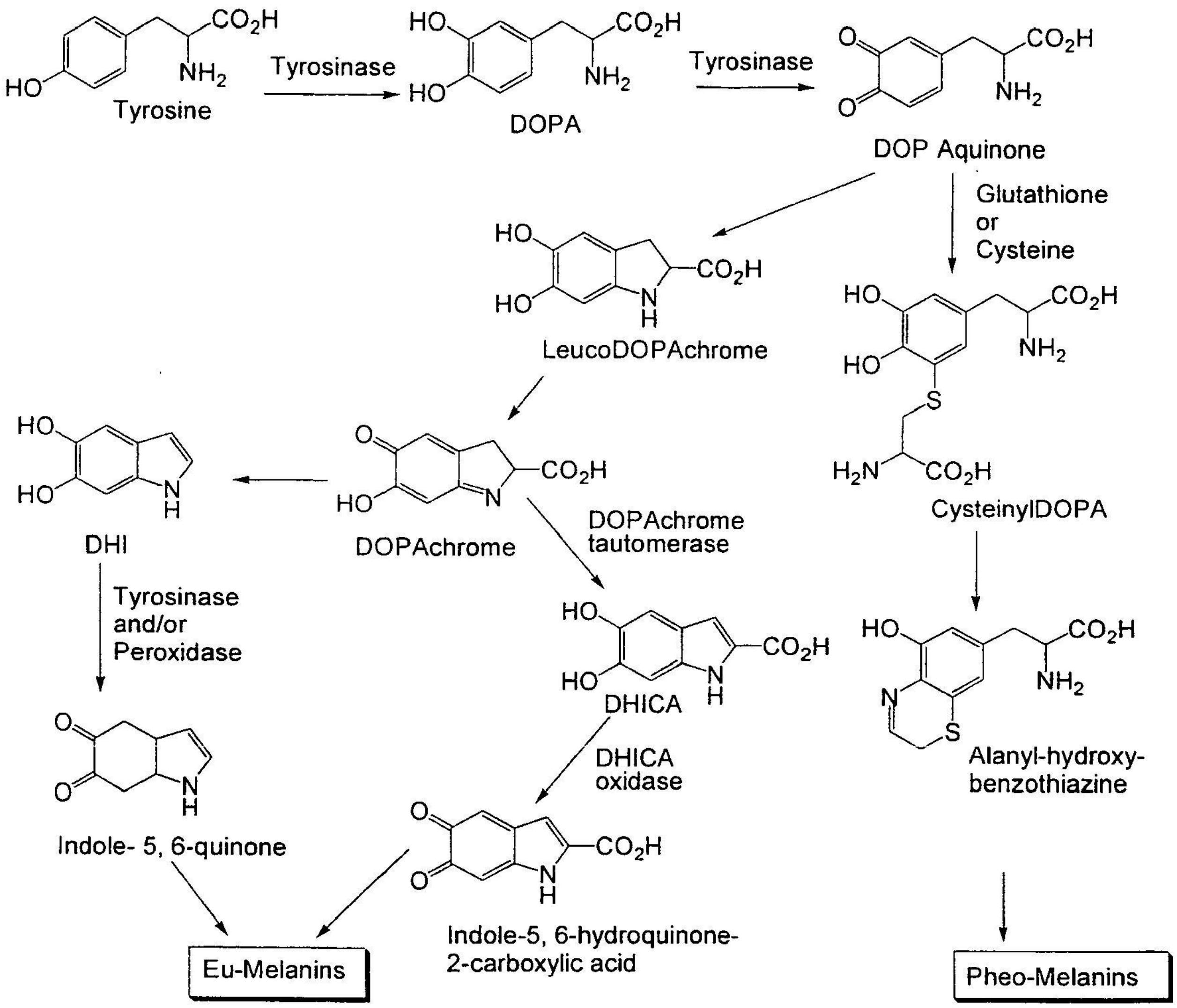
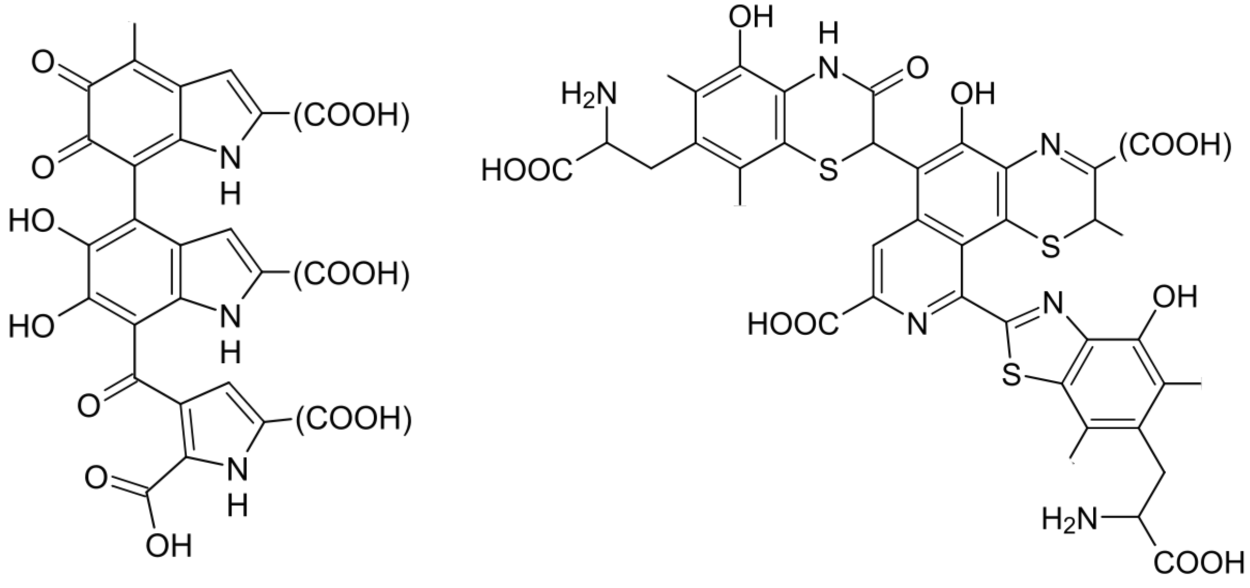


Fig. 1.2. Schematic mechanism of melanins biosynthesis.

The pigment of pheomelanin gives the fiber pinkish-red shades depending on the concentration. In sheep wool, pheomelanin is found in a small amount, in contrast to eumelanin.

Eumelanin is of two types: brown and black and differ in the structure of the polymer. A small amount of black eumelanin in the fiber, in the absence of other pigments, gives the wool a gray color, and a small amount of brown eumelanin gives yellow color.

The diversity of the initial monomers and the high activity of the intermediate products make the chemical composition of melanins diverse, and make the structure of the polymer irregular. Fragments of the structural formulas of melanins are shown in Fig. 1.3 [24, 25].



a) b)

Fig. 1.3. Fragments of the structural formulas of melanins:
a) eumelanin; b) pheomelanin.

In the structural formulas of melanins (Fig. 1.3), other substituents may be present at the site of the carboxyl group –COO, more often H.

The greater chemical stability of naturally colored fibers in comparison with white pigment-free fibers is explained by the formation of netting structures due to the interaction of melanins with sulfhydryl and amino groups of keratin.

Thus, it can be concluded that wool fiber is a natural composite material. Unlike fibers of vegetable origin, the wool has a very complex histological structure and chemical composition. The specific mechanical properties of the wool substantially depend on all levels of its structural organization, as well as on the morphology of the fiber. The presence of a scaly layer and its condition determines the technological properties of the wool, such as strength, felting, wettability, affecting the quality of finished products.

1.2. Analysis of existing methods of wool bleaching

The purpose of bleaching a wool fiber is to discolor the natural color or to eliminate the yellowness that occurs when processing or storing wool, and also to impart a higher colorability to woolen materials.

Chemical bleaching agents attack and destroy molecules of colored fiber impurities, most of which have a series of conjugated double bonds and aromatic groups as chromophores.

Traditionally, wool is bleached with the help of oxidizing and reducing agents.

1.2.1. Oxidizing methods of wool bleaching. At present, oxidizing agents based on peroxocompounds (hydrogen peroxide, peroxosulfur, peracetic, performic acid) are used for bleaching wool textile materials [29, 30]. The most widespread in the industry is hydrogen peroxide due to cheapness, ease of use and environmental friendliness.

Bleaching of wool with hydrogen peroxide is mainly produced in alkaline medium at pH 8.5-9.0. Under these conditions, there is an active bleaching agent named perhydroxyl anion ^{-}OOH:

$$H_2O_2 + OH^- \rightarrow {}^{-}OOH + H_2O.$$

An undesirable side effect is the rapid decomposition of hydrogen peroxide into water and oxygen, which is catalyzed by transition metal ions:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

The resulting gaseous oxygen has a weak bleaching effect, but can intensively oxidize peptides.

Ions of transition metals can also lead to the formation of highly aggressive hydroxyl radicals [30, 31]:

$$H_2O_2 \rightarrow 2OH^-.$$

The wool always contains a microscopic amount of ions of transition metals, in particular, iron and copper, forming a complex with fiber, which are not completely removed during washing. Thus, to prevent both these side reactions, a stabilizer is always added to the bleaching solutions, which isolates the metal ions.

Analysis of scientific and technical information [29-34] showed that the most common stabilizers for alkaline bleaching of wool for a long time were phosphates, in particular sodium tetra pyrophosphate. So when comparing three stabilizers namely sodium nitrilotriacetate, sodium diethylenetri-aminopentamethylphosphonate and stabilizer C (a mixture of sodium pyrophosphate and ammonium oxalate), it was found that the stabilizer C [32] was the most effective from the point of view of whiteness. However, concerns about the excessive release of phosphates into the environment led to the development of alternative stabilizers based on silicates [33].

After bleaching with oxidizing agents, the ability of the wool fiber to absorb the dyes increases. It is explained by the partial or complete destruction of the epicuticle and the breaking of the cross-links, leading to an increase in the ability of the fiber to swell, greater accessibility of the inner layers of the fiber. The increase in fiber availability is particularly beneficial for the absorption of slowly diffusing dyes with high molecular weight and high affinity for the fiber.

A disadvantage of the oxidative method of bleaching is the damage to the fiber, since the oxidants not only destructively affect impurity-staining fibers, but also destroy keratin. First of all, sulfur-containing groups are oxidized: cystine, methionine, lanthionine. Thus, oxidation reduces the degree of disulfide cross-linking of keratin, which leads to a loss of mechanical strength of the fiber. Peptide bonds also disintegrate, tryptophan, tyrosine, histidine, lysine, proline are destroyed [8].

It is established [34] that when dyeing of wool subjected to strong oxidative degradation, further rapid degradation of the polymer under the influence of the pH of the dye bath is possible. In this regard, dyeing in light colors, as a rule, is carried out at low temperatures 80°C, which makes it possible to achieve full absorption of the dye due to its low concentration.

To reduce the risk of fiber damage, peroxide bleaching is also carried out in a slightly acidic medium at pH 5, but the process of decolorization is slower and requires a suitable activator. According to the literature data [30, 31], an effective activator during bleaching in an acid medium is citric acid, although its mechanism of action is not clear. BASF, as an activator, patented a mixture of organic salts called Prestogen W, which generates the formation of percarboxylic acids [32].

Nevertheless, the degree of whiteness of the wool fiber after peroxide bleaching in an acidic medium is much less than after traditional alkaline bleaching [29]. Thus, peroxide bleaching in alkaline medium remains the most effective way to bleach the wool.

1.2.2. Reducing methods of wool bleaching. It is noted that the reducing agents have a softer effect on the wool fiber and, as a consequence, less damage it. In acidic and neutral media, the process ends with the formation of thiol groups. In the alkaline medium, secondary processes occur such as ionization of sulfhydryl groups, the formation of lanthionine bonds [31].

As reducing agents, stabilized sodium dithionite, commonly known as sodium hydrosulfite, and other reducing agents, including thiourea dioxide, sodium formaldehyde-sulfoxylate (rongalite), are commonly used [31, 32].

The reducing properties of thiourea dioxide are explained by the produce of sulfoxylic acid during hydrolysis. However, the authors do not exclude the negative effect on the keratin of ion-radicals SO_2 arising from the breakdown of derivatives of sulfoxylic acid [35].

The new technology of reducing bleaching of wool ("ColorClear" ™ WB) was developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO), which consists in applying the reaction of sodium borohydride with sodium bisulphite to obtain the active bleaching agent sodium dithionite in the bleaching bath [36]. Commercial tests confirmed that the technology developed is technically reliable and offers significant advantages over using conventional reducing bleaching in terms of increasing whiteness.

A disadvantage of bleaching by reducing agents is the partial loss of whiteness during washing as a result of oxidation of the reduced products with oxygen contained in water and in air.

In order to achieve a higher degree of whiteness, a two-stage process is used [37]. In the first stage, the wool is bleached with hydrogen peroxide in an alkaline medium, and then reducing bleaching is carried out, usually using sodium hydrosulfite or thiourea dioxide.

Thus, it can be concluded that wool bleaching by reducing agents is less effective than by hydrogen peroxide. Currently, reducing methods of bleaching are not widely used in industry and are rarely used without the preliminary oxidation stage of bleaching.

1.2.3. Bleaching of pigmented wool. Pigment grains that impart color to the wool are located in the internal structure of the fiber and are chemically bonded to keratin [8]. Consequently, it is almost impossible to discolor the wool without damaging it. Pigments are resistant to acids and dilute alkali solutions, but are not resistant to oxidizing and reducing agents. These properties are taken into account during bleaching of pigmented wool [32, 38-40].

It is known [38] that the pigmented wool fiber sorbs well the metal ions, in particular Fe^{2+}. This is due to the fact that hydroxyl groups appear in oxidation products of tyrosine, differing in their tendency to form complexes with metals. In this regard, effective bleaching of wool with intense natural coloration is carried out by using metal salts as catalysts for melanin discoloration [41-44].

Bleaching of pigmented wool represents a three-stage process, consisting of consecutive operations of mordanting, washing and peroxide bleaching.

The mordanting is carried out in an acidic medium, more often in the presence of reducing agents, preventing the oxidation of Fe^{2+} to Fe^{3+}. Hypophosphorous acid can be used as a mild reducing agent [41-43]. However, it should be taken into account that the presence of sulfur-containing reducing agents may promote the breaking of disulfide bonds. The use of formaldehyde as a cross-linking agent in the mordanting stage is suggested to prevent the breaking of cystine bonds [33], however, this method is not environmentally friendly.

After mordanting, a washing operation follows, the purpose of which is to remove unbound metal cations that affect the degree of fiber damage during bleaching. Cold washing practically does not remove iron ions from the fiber, so the operation must be carried out in hot water.

At the second stage, bleaching with hydrogen peroxide occurs in an alkaline medium. Discoloration of melanin is a complex process consisting of two separate stages such as oxidation of the functional groups of melanin and irreversible degradation of the polymer caused by destructive oxidation. Melanin degradation can be the result of ring-opening reactions.

Preliminary oxidation of melanin is an important step in the polymer degradation process. Such oxidation of melanin monomers can be caused by hydroxyl radicals resulting from the catalytic decomposition of peroxide under the action of metal cations:

$$\text{Mel–Fe}^{2+} + H_2O_2 \rightarrow \text{Mel–Fe}^{3+} + HO\cdot + HO^{-}.$$

Thus, the resulting hydroxyl radicals selectively affect the pigment.

It is known [39] that hydroxyl radicals react effectively with indoles. Therefore, the contribution of such processes to the discoloration of melanin can not be ruled out, since a significant number of melanin monomers refer to dihydroxyindoles and dihydroxyindole-carboxylic acids. At the same time, other fiber regions undergo normal peroxide bleaching.

It is noted that the incomplete removal of ferrous ions during the washing process can lead to the undesirable appearance of a light brown hue on the fiber due to the oxidation of Fe^{+2} to Fe^{+3} under the conditions of subsequent peroxide bleaching. In order to solve this problem, a single method of hydrogen peroxide bleaching is carried out, followed by the introduction of thiourea as a reducing agent, whereby the colored trivalent iron particles are reduced to Fe^{+2} ions, which have a lower affinity for the fiber and are easily removed by washing [40].

Thus, the discoloration of pigmented wool is a process of destruction of melanin during catalytic peroxide bleaching. Since the pigment is chemically bonded to the keratin of the wool, its destruction is associated with fiber damage. To ensure minimal damage to wool fiber during the process of discoloration, a number of parameters are very important such as the concentration of the catalyst, the pH and the temperature of the bleaching bath.

1.3. Analysis of modern directions of intensification in the field of wool bleaching

Traditional methods of wool bleaching lead to undesirable damage to the fiber and increase felting, which worsens the quality characteristics of the bleached material. In order to increase the functionality and competitiveness of bleached wool, various methods of intensifying the bleaching process are used such as biological, physical and physicochemical.

To date biotechnologies is widely used in the finishing industry. An analysis of research information has shown [45-48] that the effectiveness of hydrogen peroxide bleaching can be enhanced in the presence of proteolytic enzymes in a bleaching bath.

It is reported that peroxide bleaching in the presence of protease partially destroys cuticle cells, which positively affects the whiteness of the fiber [49]. Adding a small amount of enzyme to the bleaching bath can significantly accelerate the decomposition of hydrogen peroxide, acting as a catalyst, and thus contribute to an increase in whiteness of the fiber [50].

In a number of works [46, 47, 51] it is noted that the use of enzymes in peroxide bleaching of wool allows not only to achieve high whiteness, but also to reduce the concentration of peroxide in bleaching solutions and the duration of treatment. The activation of the process of bleaching in the presence of enzymes is explained by the fact that the number of amino groups increases as a result of hydrolysis, which in turn increases the amount of adsorbed hydrogen peroxide.

However, the process conditions are limited, since enzymatic treatment significantly reduces the strength properties of the bleached wool fiber. With increasing enzyme concentration, a significant decrease in cysteic acid in the cuticle of wool fibers is observed, due to a decrease in the sulfur content in the A-layer of the exocuticle.

In addition, it was found that under conditions of peroxide bleaching in an alkaline medium after 15 min. processing enzyme activity is sharply reduced and is about 5% of the initial.

In this connection, the authors [51] determined the optimal conditions for peroxide bleaching of wool with the use of an enzyme, according to which treatment should be carried out at pH 5.5. The enzyme is used as a catalyst in conditions of peroxide bleaching in acidic medium at low temperatures.

Thus, the use of enzymatic technologies in the bleaching of wool textile materials makes it possible to improve the quality of products and the environmental friendliness of production. The disadvantage of these intensifiers is their relatively high cost and nonuniversality.

At present, one of the promising directions is the methods of intensification, based on the application of various physicochemical effects.

Methods of wool bleaching based on processing by light of a certain wavelength are given in the scientific literature. Photobleaching occurs when the wool is irradiated with light in the wavelength range 380-600 nm, the most effective is blue light with a wavelength of 400-450 nm [52].

Launer H.F. [53] used a high-pressure mercury arc, equipped with a UV filter, for photobleaching of dry wool fabric in about 15 seconds of treatment. Other researchers [34] passed the washed wool through a conveyor system equipped with fluorescent blue light lamps. It was found that when using similar low intensity blue fluorescent lamps, photobleaching can be significantly accelerated by irradiating the wool in the presence of hydrogen peroxide at pH 10-10.5. Using a parallel irradiation with low-power fluorescent lamps, it is possible to achieve a good bleaching effect of the wool.

Millington K.R. described a continuous process of photobleaching, which included impregnation of wool fabric with oxidizing or reducing agents and subsequent irradiation with visible light of high intensity [54]. As a light source, a mercury arc was used with a filter of heat-resistant glass to attenuate ultraviolet radiation.

Titanium dioxide (TiO_2) nanoparticles, which are applied to a greasy wool fabric, are known as a photocatalyst to remove the natural yellowness under the influence of daylight [55]. To enhance the adsorption of nanoparticles, at the first stage, the fabric is treated with a protease, and then with titanium dioxide in the nanoform in the presence of citric acid. It is noted that the necessary degree of whiteness is achieved and the hydrophilicity of wool textile materials is improved.

However, to date, photobleaching of wool is not used on an industrial scale.

It is known to use ultrasound as a preliminary treatment of wool before bleaching to accelerate heterogeneous processes in the liquid phase [56]. Ultrasound is an elastic vibration, the frequency of which exceeds 15-20 kHz. The mechanism of action of ultrasonic vibrations consists in the occurrence of cavitation and microflows in solution. The structure of the liquid during the collapse of bubbles bursts, large gradients of temperatures and pressures appear on local sections. It is noted that ultrasonic treatment caused some yellowing of wool, presumably because of the action of hydroxyl radicals formed under the influence of ultrasonic cavitation. However, after bleaching, the wool fabric, which had undergone preliminary ultrasonic treatment, had a higher whiteness, as compared to the control sample.

More and more attention is paid to the methods of wool modification, which represent a directed change in the surface of a fiber with maximum preservation of its natural properties and allow to some extent to improve its technological parameters, increasing the consumer properties of bleached textile materials [57].

Traditionally, the surface of wool fiber was modified using chemical and biological substances. However, due to environmental, economic and technological factors, the most promising are the physical methods of modification. Such methods include plasma-chemical treatment.

Surface modification of wool fibers during plasma treatment is carried out by etching and oxidative modification. After plasma treatment, the scaly layer is partially destroyed to a depth of 30-50 nm, affecting the F-layer of fatty acids and the A-layer of the cuticle [58-61].

Treatment of wool fabrics with low-temperature plasma increases their capillarity and wettability with water and aqueous solutions. Also for plasma-processed textile materials, there is an increase in physicomechanical and physicochemical parameters, a change in frictional properties, an increase in adhesion characteristics, and an increase in dyeability [62].

Advantages of plasma-chemical technology include increasing productivity, reducing the length of the bleaching process. In addition, this treatment ensures high safety of keratin, as a result of which the basic physicomechanical parameters of wool are increased [63, 64].

The disadvantages of the plasma-chemical activation method include a low service life of plasma-chemical equipment and its high cost.

In recent years, new electrophysical methods of processing materials have been increasingly used in many branches of industry, and characterized by a high concentration of energy, high pressure, and temperature [65]. Such processes include a high-voltage electrical pulse discharge in a liquid, the practical application of which in the various technological processes of production was first proposed by the Soviet scientist Yutkin L.A., calling this phenomenon an electro-hydraulic effect [66]. Under his leadership, the basic designs of industrial constructions for various purposes were developed, search operations were carried out, devices and technological processes were prepared and introduced to enable the electro-hydraulic effect to be effectively used in many industries.

Scientists of the Institute of Impulse Processes and Technologies of the National Academy of Sciences of Ukraine (Nikolaev) have studied in detail the phenomenon of occurrence and development of electrical discharge cavitation at all stages of an electrical discharge in a liquid, as well as the principles of EDNBC control. A number of resource-saving technologies for deep processing of flax fiber using EDNBC have been developed [67, 68]. Optimal physical parameters of material treatment are established. Due to the complex of phenomena that arise during the generation of this process (powerful pulsed electric and magnetic fields, light radiation, low-frequency acoustic emissions, intense hydro-streams, shock waves, chemical radicals and radical groups that are formed due to decomposition of water molecules), a certain level of exposure is achieved on objects in the water.

The technology of wool fiber modification during the washing with the use of EDNBC was developed [69-71]. In the course of the work, the process of electrical-discharge treatment of wool was studied and its main technological parameters were determined. It was found that the effect of EDNBC leads to a change in the surface and supramolecular structure of the wool fibers.

In this connection, it is of interest to study the effectiveness of the use of preliminary electrical-discharge treatment as a method of surface modification of wool fiber to improve its qualitative characteristics during the subsequent peroxide bleaching in order to minimize damage to wool, improve the quality of finished products and reduce its cost price.

CONCLUSIONS TO SECTION 1

The presence of colored impurities in the wool fiber, distorting its natural color, and the presence of pigments prevents the formation of clean and bright colors during dyeing. In this regard, if you want to produce wool textile materials in both painted and pure bleached form, the wool is bleached. Traditional technologies of bleaching wool fiber lead to significant damage to the structure of keratin, which negatively affects the quality of finished products.

There are a number of ways to intensify the process of wool bleaching, but they do not always meet the requirements of a particular enterprise for technical and economic reasons. Therefore, the development of new methods of bleaching wool in order to produce high-quality bleached fiber is an urgent task.

In this regard, the main goal of the study is the development of technologies for the bleaching of wool fibers with the use of EDNBC in order to improve the quality and competitiveness of the finished product by reducing its cost.

To accomplish the stated goal, the following tasks have been set:

– to develop technologies of semi-fine wool and coarse pigmented wool bleaching with the use of electrical-discharge processing as a method of preliminary modification;

– theoretically substantiate and experimentally confirm the effectiveness of the use of preliminary electrical-discharge processing for the modification of wool fiber;

– to analyze and establish the influence of EDNBC on the surface properties of semi-fine and coarse wool, to determine the technological parameters for conducting the process of electrical-discharge processing;

– to determine the effect of preliminary electrical-discharge treatment of wool fiber on the degree of whiteness and strength after the bleaching process.

SECTION 2

OBJECTS AND METHODS OF RESEARCH

2.1. Characteristics of research objects and substances used in work

2.1.1. Textile materials. A different in color and fineness washed wool fibers (semi-fine, coarse and pigmented coarse wool) in the form of tops were selected for the study.

Semi-fine tsigay wool is characterized by uniformity, staple structure. It is white, quality 56, length II [72].

The coarse wool of the Tushinsky sheep breed consists of undulating braids, containing 44 to 74% of the down fibers, the rest being the transition and core fibers. It is white, quality 44, length I [73].

The coarse wool of the Central Russian sheep breed is characterized by the presence of braids consisting of a large number of downy fibers and transitional and ordinary fibers emerging above them. The color of the downy fibers is white, the color of the ordinary fibers is black. The color of the wool is light gray, qualities 48, length I [73].

Characteristics of the wool, which was used in the work, is presented in Table 2.1.

Table 2.1

Technological parameters of used wool

Parameter	Wool	
	semi-fine Tsigay	coarse Tushinsky
1	2	3
Average wool fineness, µm	26,80	36,10
Average length of the staple, mm	70-110	200-250
Moistness, %	12-13	15-18
Fat content, %	0,5-1,15	0,8-2,4
The content of vegetable impurities,%, not more than	1	1

Continuation of Table 2.1

The content of mineral impurities,%, not more than	2,5	3,5

2.1.2. Chemical materials. The list of chemical materials used in the work is presented in Table 2.2.

Table 2.2

Chemical materials used in the work

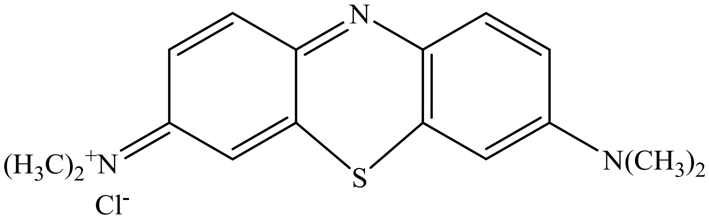
Name, chemical formula	GOST
Acetic acid (CH_3COOH)	GOST 61
Sulfuric acid (H_2SO_4)	GOST 4204
Distilled water	GOST 6709-72
Sodium carbonate (Na_2CO_3)	GOST 5100-85
Sodium hydroxide (NaOH)	GOST 4328
Carbamide (urea) ($(NH_2)_2CO$)	GOST 2081-92
Sodium hydrosulphite ($Na_2S_2O_4$)	GOST 246-76
Sodium hypochlorite (NaClO)	GOST 11087-76
Sodium sulfite (Na_2SO_3)	GOST 5644-75

The metal salts, acids and bases, which were used in the work, had the characteristics of analytic grade or high grade [74, 75].

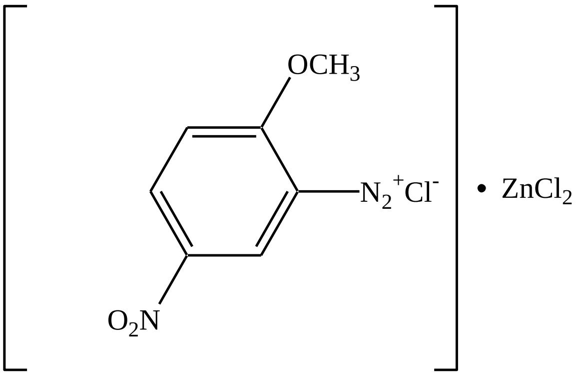
2.1.3. Dyes. Diazol scarlet R and basic methylene blue dyes were used for the study. In Table 2.3 provides basic data on the dyes used [76, 77].

Table 2.3

The structure and characteristics of the dyes used

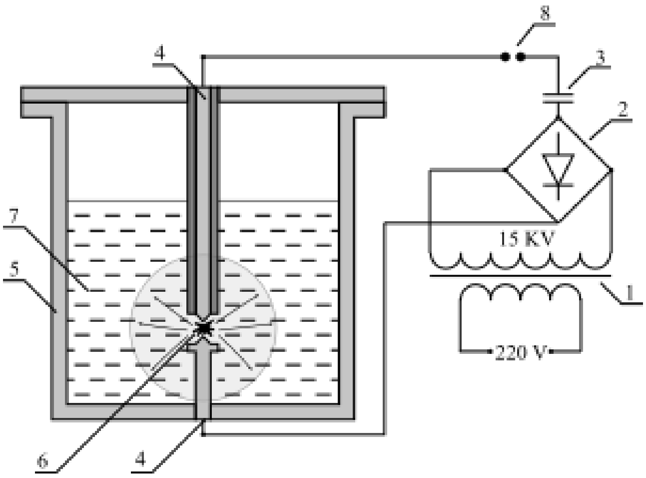
Dye	Chemical formula	Molecular weight, g/mol
Basic methylene blue		319,86

Continuation of Table 2.3

Diazol scarlet R		63,47

2.2. Methods of processing wool fibers

2.2.1. Electrical-discharge treatment of wool fibers was carried out on a laboratory setup "Vega-6", the scheme of which is shown in Fig. 2.1. The operating characteristics of the electrical-discharge equipment are shown in Table 2.4.



1 – step-up transformer;
2 – diode bridge;
3 – capacitor;
4 – electrodes;
5 – the reactor vessel;
6 – zone of discharge;
7 – liquid;
8 – air gap.

Fig. 2.1. Scheme of laboratory setup for electrical-discharge treatment "Vega-6".

Table 2.4

Equipment characteristics

Name of the parameter	Value
Frequency, Hz	50±0,1
Supply voltage, V	220±22
Efficiency, at least	0,7
Operating voltage, kV	15
Pulse repetition frequency, Hz	1,5

Continuation of Table 2.4

Capacity of the capacitor bank, uF	0,5
Power consumption, W	400

2.2.2. Chlorination. The wool was treated at a temperature of 18-20°C and a liquor ratio of 1:50 with an acidic sodium hypochlorite solution, which contains active chlorine (1 g/l), concentrated sulfuric acid (1 ml/l). The treatment was carried out for 40 min. with stirring. Then the material was washed with cold water. Then it was washed in a solution of sulfuric acid at a concentration of 5% for 2-3 min. and again with cold water. After that, for the purpose of antichlorination, the wool was treated with a solution of sodium sulfite at a concentration of 2% and a liquor ratio of 1:50, a temperature of 40°C for 15 min. The fiber was then washed and dried [78].

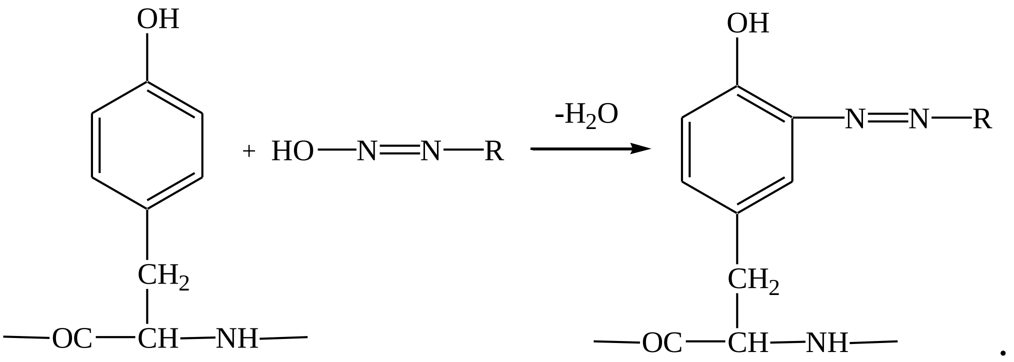
2.3. General methods and technique of researches

2.3.1. Determination of the RedOx-potential was made using a combined Combo HI 98129 tester ("HANNA Instruments"). The accuracy of measuring these values in the measured intervals was ± 0.5%.

2.3.2. Preparation of wool material for investigation and sampling was carried out in accordance with GOST 20576-88. Wool, natural sorted. Acceptance rules and methods of sampling [79].

2.3.3. Determination of the degree of damage of the fiber epicuticle was carried out with the help of the Allwörden reaction by treating wool fiber with sodium hypochlorite solution in an acidic medium. The microphotographs of the fiber surface were obtained on a microscope "Mikmed-1" with a digital camera of the DCM series and a package of applied programs.

2.3.4. Determination of the degree of damage of wool fibers by means of the diazo reaction of Pauli. The method is based on the formation of azo dye in the interaction of tyrosine of cortical layer with a diazo compound according to the scheme:



A sample of a fibrous material weighing 1 g was treated at a temperature of 20°C for 2 min. in a solution containing 0.1 g of diazol scarlet R dissolved in 25 ml of distilled water, 5 ml of a 1% solution of soda ash. The samples were then washed, dried and the intensity of their color determined. The color intensity increases in proportion to the degree of damage to the fiber. Simultaneously with the test sample, a fibrous material was treated, not subjected to damage. The degree of fiber damage was evaluated by comparing the color intensity of both samples [80, 81].

2.3.5. Determination of the degree of damage of wool fibers during dyeing methylene blue. The method is based on the ability of damaged fiber (orthocortex) to be dyed with solutions of basic dyes. A fiber weighing 1 g is dyed in a solution containing 1 g/l of basic methylene blue. The dyeing was carried out for 5 min. at a liquor ratio of 1:50 and room temperature. The samples were then washed with cold water, dried and the intensity of their color determined. The color intensity increases in proportion to the degree of damage of the fiber. Simultaneously with the test sample, a fibrous material was treated, not subjected to damage. The degree of fiber damage was evaluated by comparing the color intensity of both samples [80, 81].

2.3.6. Determination of the color intensity. The color intensity was evaluated by the reflection coefficient R% of the dyed samples and by the value of the Gurevich-Kubelka-Munk function (GKM).

Determination of the reflectance coefficients of the colored fiber was carried out on a spectrophotometer "Spekol-11" with the corresponding attachment. First, a reflectance spectrum of the textile material dyed with a certain dye is obtained. Then, the wavelength is chosen, at which the expressed minimum of the reflection coefficient is observed. At this wavelength the reflection coefficient for a given dye is determined.

The reflection coefficient is not linearly related to the concentration of the dye on the textile material, so the color intensity is better characterized by the function of the GKM, which was determined by the formula:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R^o)^2}{2R^o}, \qquad (2.1)$$

K/S is GKM function;

R and R^o are the spectral reflection coefficients of the colored and un colored textile materials, respectively [80].

2.3.7. Determination of whiteness of wool fiber was carried out according to GOST 18054-72 [82].

2.3.8. Determination of the relative breaking load of the wool staple was carried out on a dynamometer DSH-3M in accordance with GOST 20269-93. Wool. Methods for determining the breaking load [83].

2.3.9. Determination of wool solubility in 0.1 N NaOH solution. A sample of a fiber weighing 2 g, weighed accurate to the 0.0003 g, was immersed in a 0.1 N sodium hydroxide solution and held in an air thermostat for 1 hour at a temperature of 65°C and a liquor ratio of 1:50. After that, the wool was filtered, washed 10 times with water, twice with 60% acetic acid and distilled water until neutral. Then wool was dried at 105°C to constant weight. The wool solubility in 0.1 N NaOH solution (X,%) was calculated by the formula:

$$X = \frac{(m_i - m_f)}{m_0} \cdot 100, \qquad (2.2)$$

m_i – initial mass of wool fibers, g;

m_f – wool mass after NaOH effect, g;

m_0 – mass of absolutely dry sample of unaffected wool, g [80].

2.3.10. Determination of wool solubility in urea-hydrosulphite reagent. A sample of a fiber weighing 2 g, weighed accurate to the 0.0003 g, was immersed in a solution that contained 50% urea and 3% sodium hydrosulfite and held in an air thermostat for 1 hour at a temperature of 65°C and a liquor ratio of 1:50. After that, the wool was filtered, washed 10 times with water, twice with 60% acetic acid and distilled water until neutral. Then wool was dried at 105°C to constant weight. The wool solubility in the urea-hydrosulphite reagent (UHR) (X,%) was calculated by the formula:

$$X = \frac{(m_i - m_f)}{m_0} \cdot 100, \qquad (2.3)$$

m_i – initial mass of wool fibers, g;

m_f – wool mass after UHR effect, g;

m_0 – mass of absolutely dry sample of unaffected wool, g [80].

2.3.11. The average fineness of wool fiber was determined in accordance with GOST 17514-93. Wool, natural. Methods for determining the fineness [84].

2.3.12. Determination of the crimp frequency of wool was carried out according to GOST 13411-90. Fibers and tow, chemical. Methods for determining the crimp frequency [85].

2.3.13. Determination of the degree of felting of wool fiber was carried out by shaking a sample of wool in an aqueous medium. The ability to felting was evaluated by the density of the balls formed during shaking, which was calculated from its diameter:

$$V_b = \frac{1}{6}\pi d^3, \qquad (2.4)$$

$$Q = \frac{m}{V_b}, \qquad (2.5)$$

V_b – ball volume, cm^3;

d – ball diameter, cm;

Q – ball density, g/cm^3;

m – fiber weight, g [86].

2.4. Methods for processing the results of an experiment

Statistical processing of experimental data included the calculation of point and interval estimates of experimental results. At least five repetitions were carried out in each experiment. When processing experimental data, the methods of modern mathematical statistics, correlation analysis with the value of the Student's criterion corresponding to the confidence probability equal to 95% were used.

Mathematical models of the experimental curves are constructed using the PC, MS Office-2016 "Excel" and Curve Expert 1.4 software packages. To determine the accuracy of the coincidence of the experimental and theoretical data, the standard error S and the coefficient of variation R were calculated in plotting the curves.

The accuracy of the measured values was taken, respectively, in the characteristics of the measuring instruments given in the passports. The error in the process of performing analytical studies did not exceed 2% [87-89].

CONCLUSIONS TO SECTION 2

1. A different in color and fineness washed wool fibers (semi-fine, coarse and pigmented coarse wool) in the form of tops were selected as the main subjects of research. The choice of subjects of research was determined by the study of the market of production and consumption of wool textile materials, with a comprehensive account of the properties of fibers that affect the quality of finished products during their operation.
2. The results of the research should ensure the production of high-quality bleached wool and increase the competitiveness of finished products in the Ukrainian and world markets.

SECTION 3

THEORETICAL AND EXPERIMENTAL SUBSTANTIATION OF THE APPLICATION OF ELECTRICAL-DISCHARGE NONLINEAR BULK CAVITATION IN THE TECHNOLOGY OF BLEACHING WOOL FIBERS AS A METHOD OF PRELIMINARY MODIFICATION

3.1. Theoretical justification of the choice of electrical-discharge nonlinear bulk cavitation in the technology of bleaching wool fibers

The main task in the process of wool bleaching is the maximum preservation of valuable natural properties of wool fibers. However, methods of bleaching used at domestic enterprises do not always allow to provide the required quality of bleached wool. The main problems in the classical wool bleaching technology are a significant degradation in the mechanical properties of the fiber due to destruction and increased felting, which affects the efficiency of the spinning and weaving processes. In addition, a fiber that is severely damaged during bleaching becomes more prone to hydrolysis under the influence of the temperature and pH of the dye bath during subsequent dyeing [8].

Nowadays, an effective way to increase the functionality and competitiveness of manufactured wool products can be a modification of the wool, which is a directed change in the surface of the fiber to improve its performance properties [90, 91].

Since in modern conditions it is economically expedient to develop combined methods for changing the properties of the wool fiber surface with the main technological finishing processes, the main task in this work was the search for a method of modification of the wool during its bleaching, which will allow to impart the necessary properties to the fiber-forming polymer and, at the same time, to minimize the loss of mechanical strength of the fiber.

It is known that the process of wool fiber modification is carried out by chemical, biochemical or physical methods [92]. In recent years, special attention has been paid to physical methods of influence on fiber [93].

Analysis of the scientific and technical literature [94-101] shows that one of the promising directions of modifying the surface of fibers is recognized the processes based on the use of electrophysical influences, as the most effective, economical and environmentally safe. Such processes include high-voltage electric discharge in the liquid, accompanied by the appearance of EDNBC. The principal possibility of using the electrical-discharge effect in the technological processes of washing and dyeing of wool fibers has been proved [70, 71, 102]. It is established that the influence of the active factors of EDNBC on wool during washing leads to a change in its physico-mechanical, technological, sorption and chemical properties without a significant destruction of the keratin structure [110]. In this connection, it was of interest to study the effectiveness of the use of preliminary electrical-discharge treatment as a method for surface modification of wool fiber to reduce the loss of its mechanical strength and reduce the felting during the subsequent peroxide bleaching.

In the process of electrical-discharge treatment, the wool is subjected to simultaneous physical and chemical effects. The main acting factors that have the most significant effect on the process of wool fiber modification are the direct impact of the electrohydraulic shock, as well as the products of water breaking, formed in the working medium under the action of cavitation [103].

Under the action of hydraulic shocks due to the pulse-generated high pressure resulting from the collapse of the cavitation cavities, the surface of the wool fiber is smoothed and the supramolecular and pore structure is modified [112].

Data presented in the scientific and technical literature [94, 103, 105, 106], characterizing the chemical transformations in water during its cavitation treatment, indicate a change in its physico-chemical properties. The total reaction of formation of free radicals and their recombination in water under the influence of cavitation is presented in the following form:

$H_2O \Rightarrow H_2O^*, H^\circ, OH^\circ, H_2, HO_2^\circ, H_2O_2$ [103]. It was found that under the action of EDNBC, water molecules are restructured and activated, free radicals and their recombination products are formed, and the pH and conductivity of water increase [107].

Thus, it can be concluded that cavitation activates complex physicochemical processes in the working medium. The formation of products of water breakdown and their compounds is accompanied by oxidation-reduction reactions. The measure of the chemical activity of elements in chemical reactions is the oxidation-reduction (redox) potential. The value of redox potential is closely interrelated with the nature of the change in the properties of the processed material. Wool, which has a complex chemical and physical structure, is very sensitive to the action of oxidants and reducing agents, which actively affect, first of all, the surface of the fiber, the state of which determines its main technological and consumer properties.

In connection with the foregoing, it was of interest to study the change in the redox potential of the working medium in the process of electrical-discharge treatment. Settled water was subjected to electrical-discharge treatment at the "Vega-6" device with constant values of voltage and pulse frequency with varying duration of exposure. The dynamics of the redox potential change during 180 s with the electrical-discharge treatment is shown in Fig. 3.1.

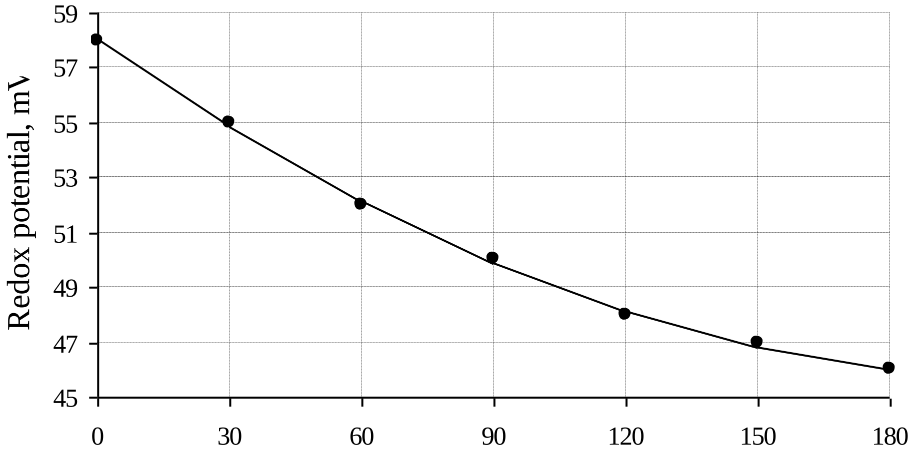


Fig. 3.1. Effect of the duration of the electrical-discharge treatment on the change in the redox potential of water:

$y = 58{,}048 - 0{,}114x + 0{,}0003x^2$, $S = 0{,}1543$; $r = 0{,}9996$.

The analysis of the presented results (Fig. 3.1) indicates a decrease in redox potential with an increase in the treatment time, which is consistent with the previously established data, according to which the pH of the medium increases during electrical-discharge treatment. Thus, during the first minute of treatment, the redox potential is reduced by 10%. Further, a less intensive change in the indicator is observed. For 3 min. of cavitation treatment, the decrease in redox potential is 21%. It is obvious that the decrease in the redox potential values during the process of electrical-discharge treatment of water is due to the formation of hydrogen atoms and hydrated electrons, which are active reducing agents.

Chemical processes occurring in the aqueous medium after the cessation of the cavitation effect, are most difficult, since during this period various chemical compounds that have arisen during the entire treatment stage come into contact.

Therefore, in the next stage of the work, a study was made of the effect of subsequent relaxation on the redox potential of water, which was subjected to electrical-discharge treatment of various durations. The experimental results in the form of graphical dependences of the redox potential value on the relaxation time are shown in Fig. 3.2.

The graph (Fig. 3.2) shows the most intense decrease in the redox potential for the first day after the effect of cavitation. Moreover, the rate of change of this parameter increases with the duration of the cavitation action, which is explained by the greater concentration of active particles in the water. With the passage of time, this relationship persists. In general, the stage of water relaxation after the action of EDNBC is characterized by a long duration and a decrease in the redox potential values to negative values.

Based on the obtained results of the study, it can be concluded that the chemical processes that occur during the electrohydraulic action on water during the treatment of wool fibers will be predominantly of a reducing nature.

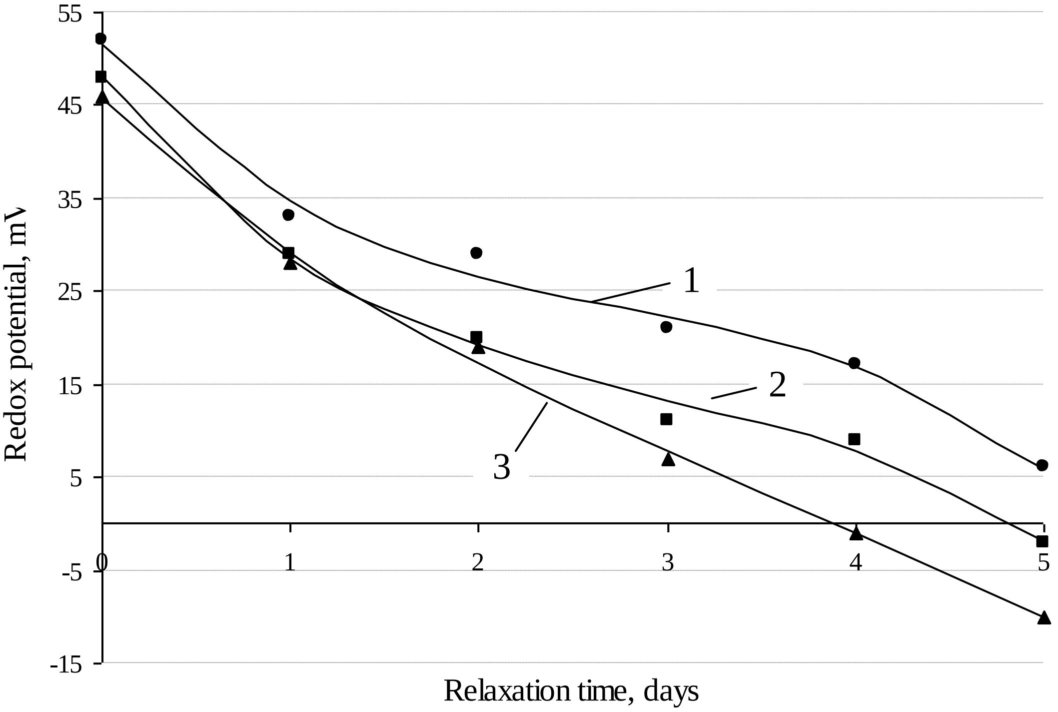


Fig. 3.2. Effect of the relaxation time on the redox potential of water after the electrical-discharge treatment:

1 – electrical-discharge treatment during 60 s:

$$y = 51{,}532 - 22{,}652x + 6{,}687x^2 - 0{,}796x^3,\ S = 2{,}3111,\ r = 0{,}9957;$$

2 – electrical-discharge treatment during 120 s:

$$y = \frac{48{,}132 - 9{,}864x}{1 + 0{,}444x - 0{,}104x^2},\ S = 1{,}9170,\ r = 0{,}9976;$$

3 – electrical-discharge treatment during 180 s:

$$y = \frac{45{,}790 - 11{,}758x}{1 + 0{,}199x - 0{,}028x^2},\ S = 1{,}5275,\ r = 0{,}9989.$$

The reactions of keratin that occur during electrical-discharge treatment in an aqueous medium are of particular interest in view of the large amount of cystine bonds especially sensitive to the action of various reducing agents. However, in the process of electrical-discharge treatment, it is impossible to completely separate the physical and chemical effects on the material being processed, since the effect of modification is due to the simultaneous action of electrohydraulic shock and chemical processes in the water. A presumptive mechanism for the modification of wool fiber during its preliminary electrical-discharge treatment, which takes into account the complex influence of the main factors of the EDNBC, is shown in Fig. 3.3.

The disulfide bonds –CH_2–S–S–CH_2–, formed during the oxidation of two cysteine residues, are covalently bound both of two different polypeptide chains (Fig. 3.3a) and various parts of one chain, which leads to the formation of loops in it (intrachain interaction). It is known that cross cystine bridges between polypeptide chains are restored more easily than intrachain bridges [8, 108, 109]. To initiate the rupture of the cystine bridges, a small amount of a reducing agent is sufficient, since after starting this reaction proceeds through a stepwise mechanism.

We assume that under the influence of atomic hydrogen formed in water during the electrical-discharge treatment of wool fiber, interpeptide disulfide bonds split and cystine passes into cysteine (Fig. 3.3b).

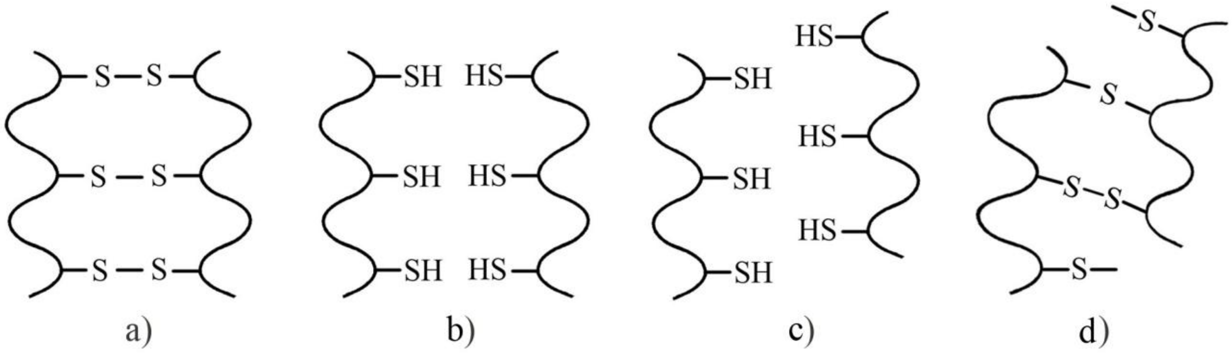


Fig. 3.3. Presumptive mechanism of wool fiber modification in the process of electrical-discharge treatment:
a) original polypeptide chains;
b) reduction of disulfide bonds;
c) displacement of polypeptide chains;
d) the formation of new cross-links between displaced polypeptide chains.

In addition, polypeptide chains with reduced cystine bonds can freely move relative to each other under the influence of electrohydraulic impact (Fig. 3.3c). Under the action of oxidants present in the working medium, the sulfhydryl groups of cysteine can easily be oxidized again, forming new cystine bonds. In addition, under conditions of cavitation treatment, reactive SH–groups can enter into chemical interactions, forming other stronger cross lanthionine bonds –CH_2–S–CH_2– (Fig. 3.3d).

Thus, it can be concluded that in the process of electrical-discharge treatment with the complex influence of EDNBC, the disulfide bonds of keratin of wool will change, which will lead to a change in its native properties. So the formation of new cross-links in the keratin will lead to an increase in strength, increase resistance to hydrolysis, the action of oxidants and reducing agents, as well as a decrease in the tendency to fiber felting.

This circumstance suggests that the use of EDNBC as a method of preliminary modification of wool fiber will help improve its mechanical and technological properties during subsequent bleaching.

3.2. The study of the effect of electrical-discharge nonlinear bulk cavitation on the surface of wool fiber

It is known that most methods of chemical, physical and biological modification lead to a significant decrease in the mechanical strength of the wool due to damage of the cuticle of the fiber [110, 111]. In addition, the state of the fiber cuticle largely determines a number of the most important technological and consumer properties of wool, such as the ability to felting, wetting by water and technological solutions, the rate of diffusion of dyes, etc.

The different content of amino acids in whole wool fiber and its histological elements determines the peculiarities of its chemical, and, consequently, technological properties. Sulfur-containing amino acids cysteine and cystine are important because they participate in the formation of disulfide bonds, which increase the strength characteristics of wool fibers and their chemical resistance to the action of various reagents [8, 9, 17].

The amino acid composition of the cuticle, which is about 10% of the fiber mass, is characterized by the highest content of cystine [11, 17]. Cuticle cells also have a high content of cysteic acid, serine, proline, glycine and valine.

The main part of cuticle cells consists of two separate layers namely exocuticle and endocuticle, differing in the content of cystine (Fig. 3.4) [19, 112, 113].

Each cell of the cuticle is surrounded by a thin protein membrane named epicuticle, which is a protective layer of about 2-7 nm thick and is about 0.1% of the total weight of the fiber. The fatty acids layer (F-layer), covalently bonded to the epicuticle, causes the hydrophobic properties of the wool fiber surface [114, 115]. Epicuticle has a high resistance to the action of chemical reagents, which is explained by the existing interaction between lipids and proteins.

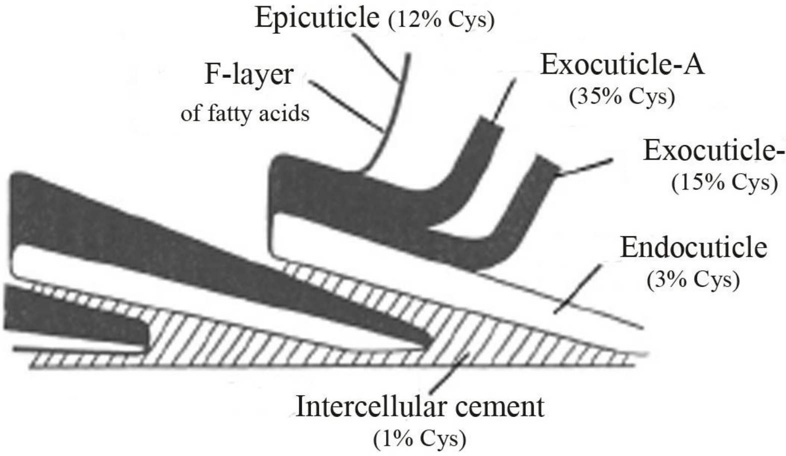


Fig. 3.4. Scheme of the structure of the cuticle of wool fiber.

Immediately beneath the surface membrane is the exocuticle, which is divided into two subcomponents: an outer A-layer containing 35% cystine, and an inner B-layer containing 15% cystine. Thus, exocuticle, which accounts for about 60% of the total cuticular layer, is characterized by the highest sulfur content, which causes a high density of cross-linking of the peptide chains [8, 9]. It is known that the exocuticle contains one transverse linkage for every five amino acid residues, which is twice the density of the cross-linking of the entire wool fiber [11].

Based on the above, it can be concluded that the integrity of the outer layer of the exocuticle is the determining factor in the strength characteristics of wool fibers. It is known that electrical-discharge treatment leads to smoothing of the surface of wool fiber without significant destruction of the cuticle structure [116].

In this connection, it was of interest to determine the depth of the effect of EDNBC on the surface of a wool fiber by examining the state of the protective top layer of the cuticle. The epicuticle can be defined as a membrane that rises in the form of bubbles or pouches along a wool fiber immersed in chlorine water. This phenomenon is called the Allwörden reaction. When the wool fiber is treated with chlorine water, the proteins of the underlying A-layer of the exocuticle dissolve under a stable membrane of the epicuticle. Reactions include oxidation of disulfide bonds of cystine and cleavage of peptide bonds in tyrosine residues [117]. As a result of the fact that the water-soluble peptide fragments are not able to diffuse through the semipermeable epicuticle membrane, a large amount of water is absorbed. The increase in osmotic pressure results in the extension of the epicuticle membrane to the outside. Since the characteristic for this reaction bubbles are formed only on the outer surface of cuticle cells and are not formed on cortex cells, this experiment can be used to study the degree of epicuticle damage [118].

Semi-fine wool after electrical-discharge treatment for 180 s was subjected to the study. For comparison, chemically modified (chlorinated) fiber was also treated with chlorine water. Micrographs of wool samples after treatment with chlorine water are shown in Fig. 3.5.

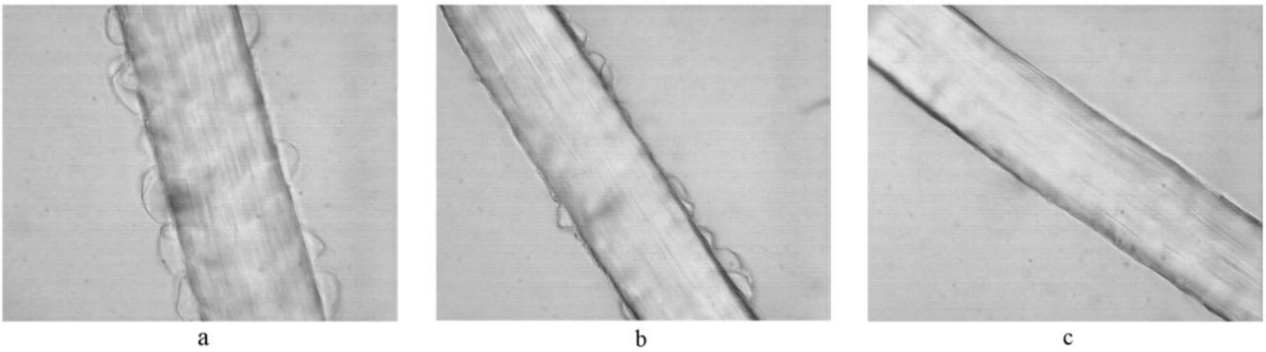


Fig. 3.5. Influence of the modification method on the damage of epicuticle of wool fiber:

a) without treatment;
b) electrical-discharge treatment;
c) chlorination.

The initial wool fiber is characterized by the integrity of the cuticular layer, therefore gives a positive reaction of Allwörden, expressed in the formation of regular and almost continuous bubbles (Fig. 3.5a).

Fig. 3.5b shows the formation of bubbles characteristic for this reaction on wool fiber after electrical-discharge treatment, which indicates the preservation of a significant part of the epicuticle after exposure to EDNBC.

To obtain bubbles, a high concentration of cysteine under the epicuticle is necessary to form soluble sulphonic acid residues [117, 118]. However, it should be borne in mind that the modification of disulfide bonds may prevent the formation of bubbles, presumably because chlorine water is not capable of oxidizing stronger crosslinks to sulphonic acid residues.

In Fig. 3.5c for chemically modified wool, the Allwörden reaction is not observed, which clearly confirms the removal of the bulk of scales from the surface of the fiber during chlorination.

The established fact of integrity of a significant part of the epicuticle in the process of electrical-discharge treatment allows us to conclude that the effect of EDNBC is directed mainly on the destruction of the hydrophobic lipid layer, which leads to an increase in wettability of the wool fiber.

Further, the degree of destruction of the cuticle of the modified wool was evaluated by coloristic methods such as dyeing with the basic methylene blue and the diazo reaction of Pauli. The results of the dependence of the color intensity of the wool on the method of fiber modification are presented in Table 3.1.

Table 3.1

The influence of the modification method on the intensity of the dyeing of wool fiber by specific dyes

Modification method	Function values K/S	
	diazol scarlet R	basic methylene blue
Initial sample	5,29	24,01
Electrical-discharge treatment	2,205	6,609
Chlorination	12,91	49

The results of dyeing with diazol scarlet R (Table 3.1) show that after electrical-discharge treatment, the color intensity is significantly reduced in comparison with the initial sample, in contrast to the intensity of the color of the fiber after chlorination. It is known that the azo dye is formed by the reaction of a diazo compound with tyrosine.

According to the literature [8, 9, 17], the greatest amount of tyrosine is contained in the intercellular substance separating the cuticle from the cortex and surrounding, in turn, each cortex cell.

Thus, it can be concluded that the decrease in the intensity of the color after the electrical-discharge treatment is due to the denser adherence of scales to the surface of the fiber, which prevents the reaction of the azo dye with the tyrosine of the cell membrane complex.

Data on methylene blue dyeing (Table 3.1) show a decrease in the value of the K/S function of the sample after the electrical-discharge treatment compared to the initial and chlorinated, which indicates the integrity of the cortical layer of the modified fiber. Reduction of the intensity of the color compared to the initial sample can be explained by the fact that the compacted under the action of EDNBC scaly layer prevents the penetration of the reagent to the cortex.

Thus, based on the results of the conducted studies, it was determined that the electrical-discharge treatment mainly affects the surface layer of the cuticle, which indicates the effectiveness of the application of EDNBC as a method of preliminary modification of wool fibers during its bleaching.

3.3. Determination of optimal parameters for electrical-discharge processing wool fibers during the modification before bleaching

Conditions that determine the shape and speed of chemical reactions accompanying the electrohydraulic action on the medium to be treated and the wool fiber placed in it can be factors such as the nature and duration of the operating forces. This indicates the importance of selecting the optimal operating mode of electrohydraulic devices for various stages of processing wool fibers.

In our opinion, in order to determine the most effective mode of electrical-discharge treatment of wool fiber for its subsequent bleaching, it is necessary to study the effect of the duration of the action of the EDNBC on the physico-mechanical (whiteness, relative breaking load, fineness, crimp) and chemical (solubility in alkali and UHR, dyeability by specific dyes), as the quality of the bleached wool material depends on the characteristics of the initial fiber.

Since the wool fiber is characterized by a complex histological structure, the EDNBC affects the wool of various fineness in different degrees [119]. In addition, the study of the process of modification, including coarse fiber, is of interest, since the improvement of its physico-mechanical properties will allow it to be used for the production of high-quality textile materials. Therefore, the determination of the optimal parameters of the electrical-discharge treatment of wool fibers for the purpose of its modification before bleaching was carried out for both semi-fine wool and coarse wool.

3.3.1. Selection of optimal parameters of electrical-discharge treatment for the modification of semi-fine wool fiber. The semi-fine wool in the form of roving, washed according to classical technology, was used as the object of research at this stage of the work, and having a homogeneous structure for obtaining reproducible results. Electrical-discharge treatment of wool fiber was carried out in tap water at a temperature of 25°C, liquor ratio of 1:150 with a variation in treatment time from 30 to 300 s. The effectiveness of the effect of EDNBC on the physicomechanical properties of wool was evaluated in a comprehensive manner in terms of the increase in whiteness and the relative breaking load.

In Fig. 3.6 shows the effect of the duration of the electrical-discharge treatment on the degree of whiteness of the washed wool roving.

The presented data (Fig. 3.6) show that the electrical-discharge treatment contributes to the increase in the whiteness of the initial wool fiber, due to the removal of residual fatty impurities from the surface of the fibers, as well as the cuticle cell membrane lipids, which give the fiber a yellow hue. The maximum increase in whiteness from 32.5 to 37% is observed after 180 s of treatment. As the time of electrical-discharge treatment increases to 300 s, there is a slight decrease in the degree of whiteness, which can be explained by the resorption of residual impurities of wool fibers removed during treatment.

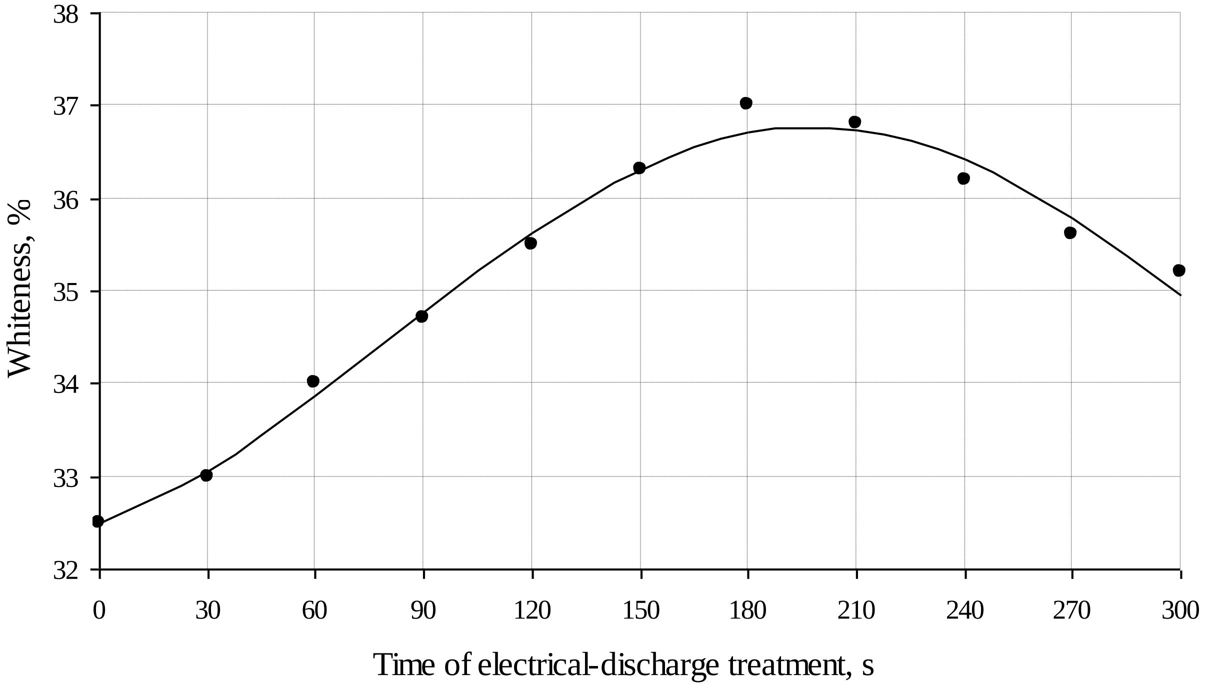


Fig. 3.6. Influence of the duration of electrical-discharge treatment on the whiteness of semi-fine wool fiber:

$y = 34{,}520 + 2{,}256 \cdot \cos(0{,}013x - 2{,}675)$, $S = 0{,}2000$, $r = 0{,}9936$.

In addition to whiteness, an important indicator of the quality of wool fibers is also its strength, which can be estimated by the index of the relative breaking load, solubility in chemical reagents and the value of dyeability by specific dyes. The dependence of the relative breaking load of wool fiber on the time of electrical-discharge treatment is shown in Fig. 3.7.

Analysis of the data in Fig. 3.7 shows that electrical-discharge treatment leads to an increase in the mechanical strength of semi-fine wool fiber, which indicates the preservation of peptide bonds in the main chains and the formation of new intermolecular bonds in keratin. The maximum increase in the relative breaking load by 13.5% is observed after 180 s of treatment.

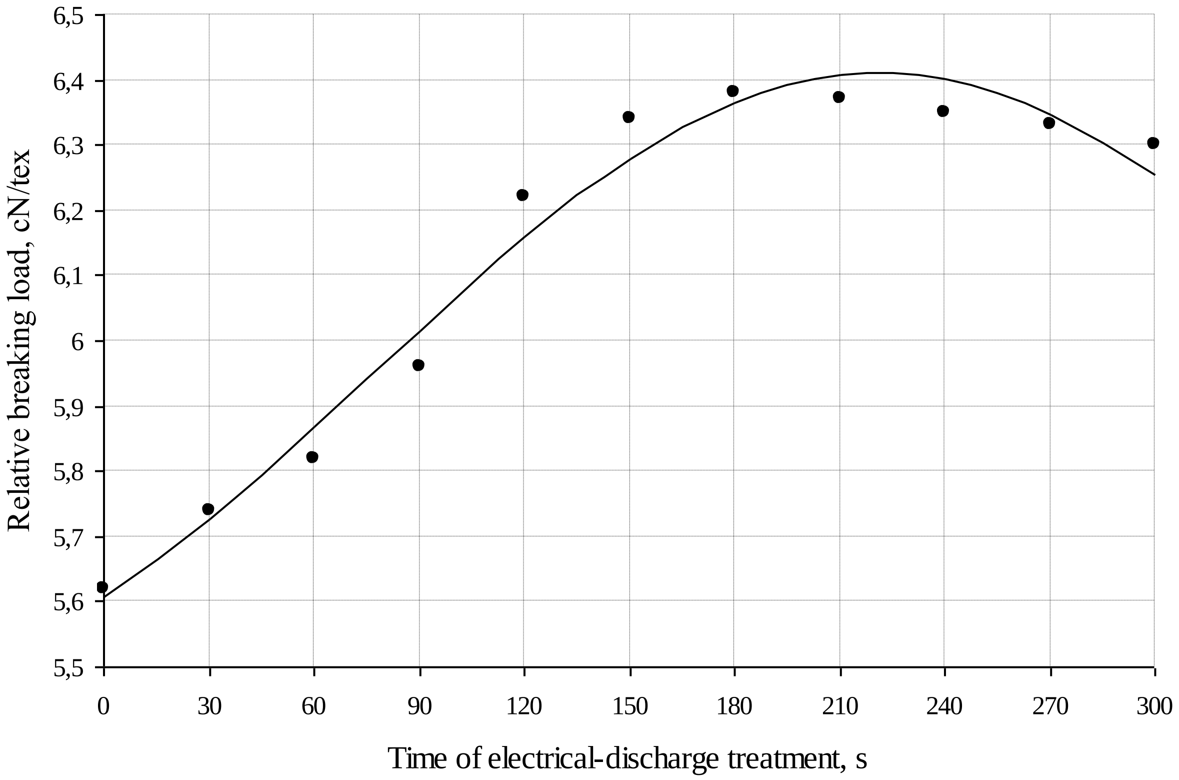


Fig. 3.7. Influence of the duration of the electrical-discharge treatment on the index of the relative breaking load of semi-fine wool fiber:

$y = 5{,}948 + 0{,}462 \cdot \cos(0{,}011x - 2{,}394)$, $S = 0{,}0534$; $r = 0{,}9879$.

Since the integrity of the wool fiber is an important characteristic of the modified wool, in the next stage of the work, a study was made of the degree of fiber damage in the dynamics of the modification process. To assess the degree of damage to wool fiber, methods based on changes in the solubility of wool keratin in chemical solutions, as well as methods using specific dyes, were used.

The solubility of wool fiber in sodium hydroxide solution characterizes the degree of hydrolysis of the main polypeptide chains. The effect of treatment time on the alkaline solubility of wool is shown in Fig. 3.8.

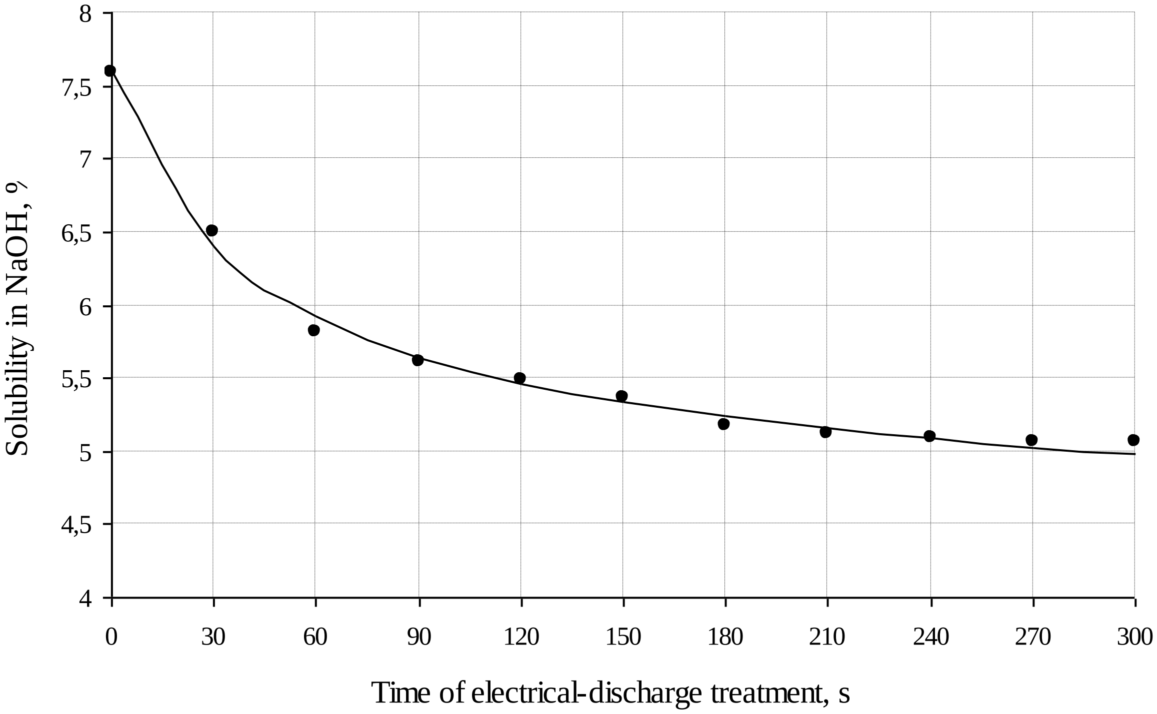


Fig. 3.8. Effect of the duration of the electrical-discharge treatment on the alkaline solubility of semi-fine wool fiber:

$$y = \frac{7{,}603 + 0{,}123x}{1 + 0{,}025x + 0{,}000004x^2},\ S = 0{,}0707,\ r = 0{,}9971.$$

The obtained experimental data (Fig. 3.8) show that the electrical-discharge treatment reduces the alkaline solubility of the wool, which indicates the high stability of the polypeptide chains to hydrolysis. The reason for increasing the resistance of keratin to the action of alkalis is the formation of new cross-links in the process of modification in accordance with the proposed mechanism of action of EDNBC on the wool of Fig. 3.3.

By the solubility of wool fibers in UHR, one can judge the number of cross-links in keratin. However, it is necessary to take into account the sensitivity of this method to factors not related to fiber damage. The dependence of wool solubility in UHR on the duration of the electrical-discharge treatment is shown in Fig. 3.9.

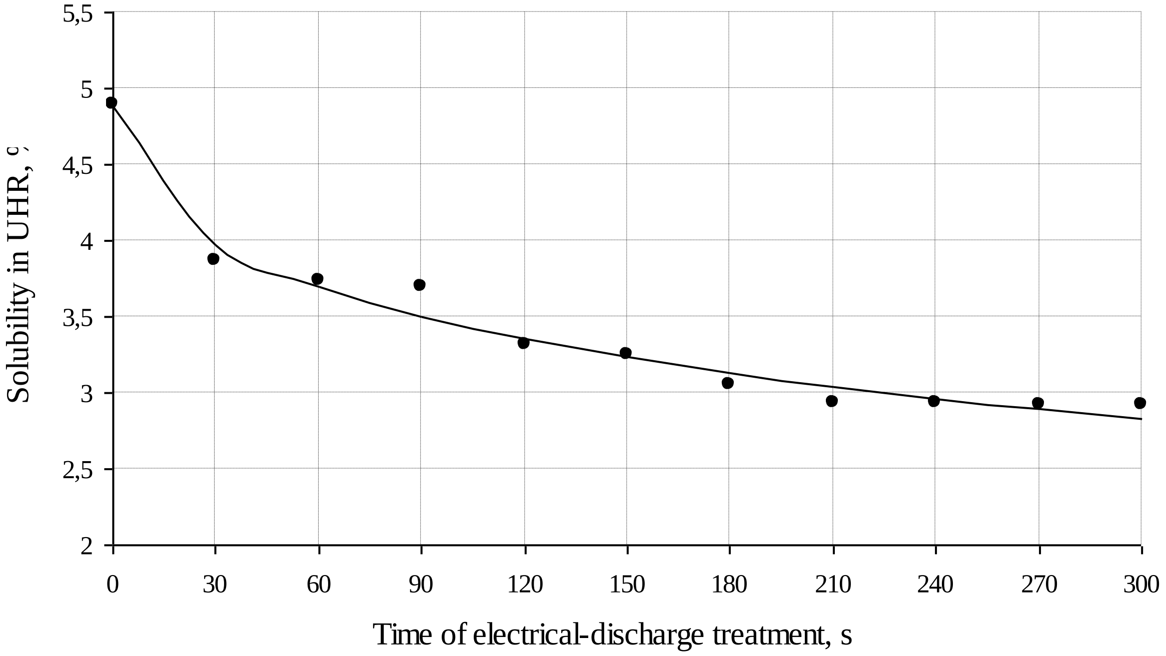
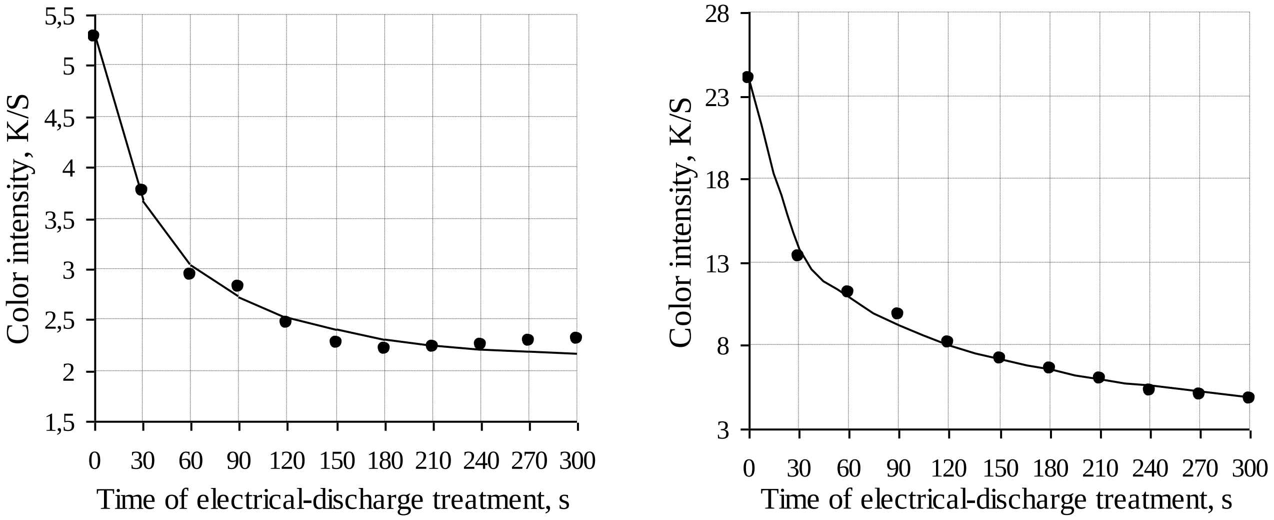


Fig. 3.9. Effect of the duration of the electrical-discharge treatment on the solubility of semi-fine wool fiber in UHR:

$$y = \frac{1}{0{,}205 + 0{,}008x^{0{,}501}}, \quad S = 0{,}1028, \quad r = 0{,}9885.$$

The results shown in Fig. 3.9, show that with increasing treatment time, a decrease in wool solubility is noted, which can be explained by the conversion of a part of the cystine bonds into lanthionine bonds, which are not hydrolyzed in UHR (Fig. 3.3).

Investigation of the effect of modification on the degree of damage to wool fiber was also carried out by color methods. It is known that the dyeing of wool by diazol scarlet R is an indirect evaluation of the degree of damage to the scaly fiber layer, and dyeing with the basic methylene blue is a characteristic of the degree of damage to the cortical fiber layer. The results of the effect of the duration of the electrical-discharge treatment on the value of dyeability by specific dyes are shown in Fig. 3.10.



a) b)

Fig. 3.10. Influence of the duration of electrical-discharge treatment on the color intensity of semi-fine wool fiber:

a) Diazol scarlet R: $y=\dfrac{5{,}306+0{,}040x}{1+0{,}026x-0{,}00001x^2}$, $S=0{,}1175$, $r=0{,}9947$;

b) Basic methylene blue: $y=\dfrac{1}{0{,}042+0{,}003x^{0{,}721}}$, $S=0{,}3703$, $r=0{,}9983$.

The results of dyeing with diazol scarlet R (Fig. 3.10a) after electrical-discharge treatment show that in the time interval from 30 to 180 s the intensity of the color decreases, which indicates the densification of the surface structure of the fiber. A longer exposure to EDNBC during 210-300 s does not lead to an increase in the effect of modification.

In the case of dyeing with methylene blue (Fig. 3.10b), the values of the K/S function decrease compared to the untreated sample in the entire time interval of the electrical-discharge treatment, which is explained by the difficulty of the reaction of the basic dye with the cortex due to the compaction of the scaly layer. It should be noted that after 180 s of exposure the color intensity changes to a lesser extent.

Analysis of the results of the determination of the effect of the duration of the action of EDNBC on whiteness, relative breaking load, solubility in NaOH and UHR, and also on the dyeing with specific dyes allowed to determine that the optimum time of electrical-discharge treatment is 180 s at which the maximum increase of whiteness and strength is achieved.

In Table 3.2 shows the results of changes in the physico-mechanical and chemical properties of semi-fine wool fiber before and after electrical-discharge treatment for 180 s. In addition, technological properties (fineness, crimp, felting) of modified semi-fine wool were determined.

Table 3.2

Change in physical, mechanical, chemical and technological properties of modified semi-fine wool fiber

Parameter		Fiber	
		untreated	modified
Whiteness, %		32,5	37
Relative breaking load, cN/tex		5,62	6,4
Solubility in technological solutions, %	NaOH	7,5	5,5
	UHR	4,9	3,1
Intensity of coloring with specific dyes, K/S	Diazol scarlet R	5,29	2,205
	Basic methylene blue	24,01	6,609
Average fineness, µm		26,80	25,53
Crimp, %		15,45	18,30
Degree of felting, g/cm^3		0,109	0,088

Thus, it has been established that electrical-discharge treatment for 180 s leads to an improvement in the quality of the fiber namely an increase in whiteness and relative breaking load, a decrease in the solubility in sodium hydroxide and UHR, as well as the color intensity of diazol scarlet R and basic methylene blue. It should also be noted that under the selected conditions of electrical-discharge treatment, the technological properties of the semi-fine wool are improved namely decrease the felting and increase crimps with a slight decrease in the fineness of the fiber.

3.3.2. Selection of optimal parameters of electrical-discharge treatment for the modification of coarse wool fiber. It is known that the influence of EDNBC is more pronounced on coarse wool due to the peculiarities of its histological structure [102, 104, 119]. Washed coarse wool in the form of roving was subjected to the study. Electrical-discharge treatment of wool fiber was carried out in tap water at a temperature of 25°C, liquor ratio of 1:150 with a variation in treatment time from 30 to 180 s.

In Fig. 3.11-3.14 depicts the dependences of whiteness, relative breaking load, solubility in alkali and UHR, as well as the dyeability by specific dyes on the treatment time.

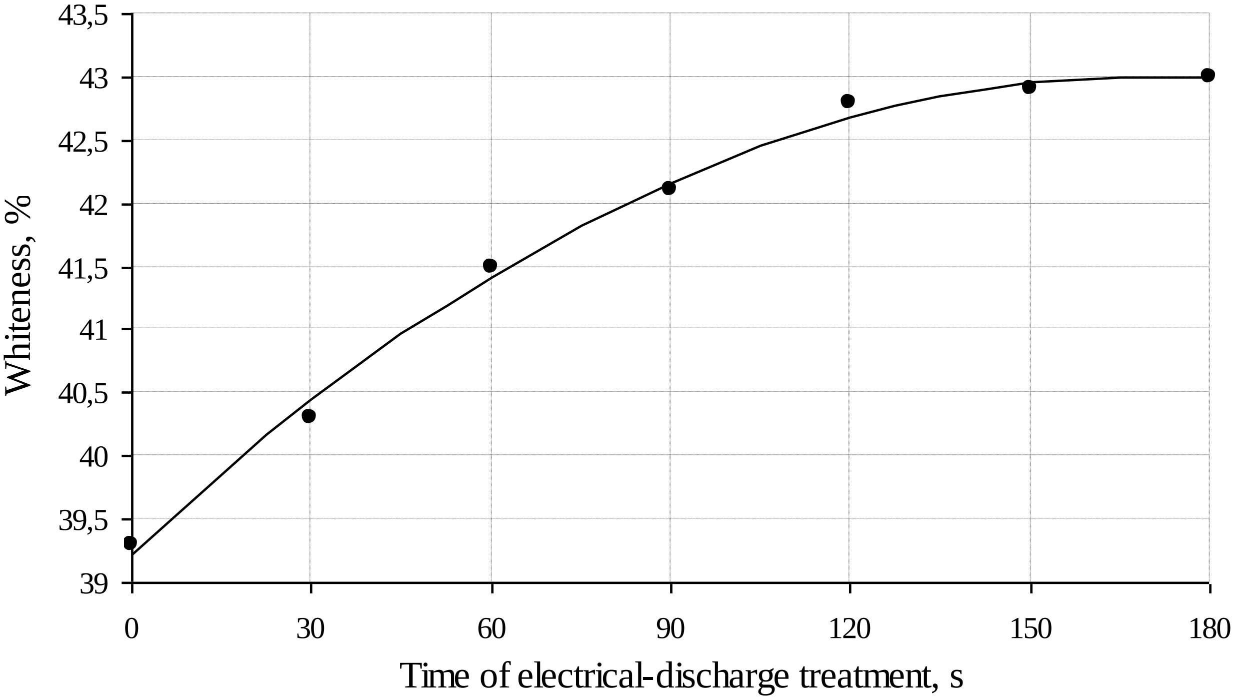


Fig. 3.11. Effect of the duration of the electrical-discharge treatment on the whiteness of coarse wool fiber:

$$y = 39{,}231 + 0{,}044x - 0{,}0001x^2,\ S = 0{,}1160,\ r = 0{,}9978.$$

The results shown in Fig. 3.11 indicate that EDNBC has a positive effect on the degree of whiteness of coarse wool fiber. For 180 s the treatment, the studied indicator rises from 39.3% to 43%.

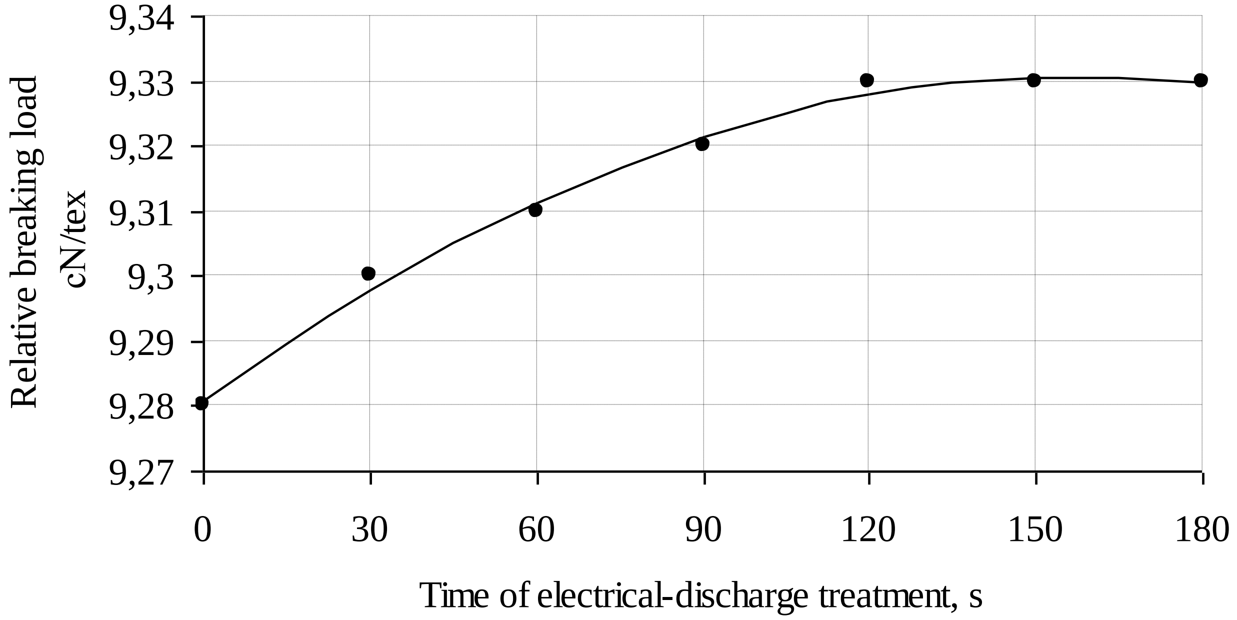
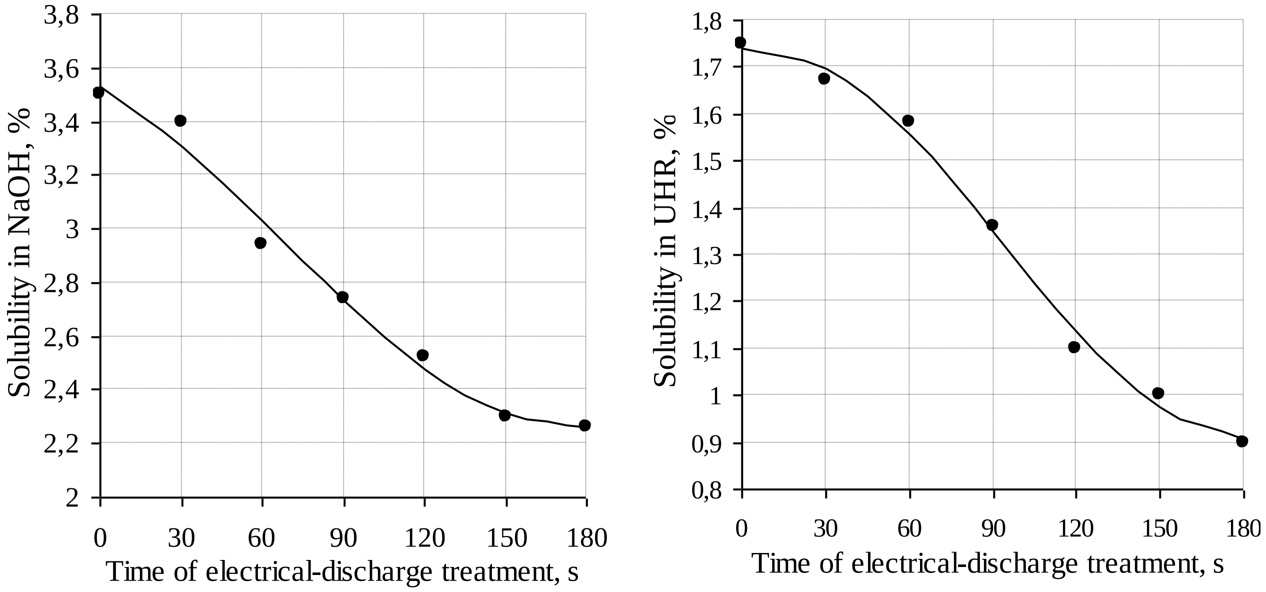


Fig. 3.12. Influence of duration of electrical-discharge treatment on the relative breaking load of coarse wool fiber:

$y = 9{,}281 + 0{,}0006x - 0{,}000002x^2$, $S = 0{,}0019$, $r = 0{,}9967$.

Analysis of the data in Fig. 3.12 shows that the electrical-discharge treatment leads to an increase in the mechanical strength of coarse wool fibers. It should be noted that under the influence of EDNBC the relative breaking load of coarse fiber changes less intensively, compared to the results of a similar study on semi-fine wool, with the maximum increase of this index being achieved in 120 s of treatment.

The data presented in Fig. 3.13 indicate that the electrical-discharge treatment of coarse wool fiber helps to reduce the degree of hydrolysis of the main polypeptide chains of keratin due to the formation of stronger cross-links, which agrees with the results of studies carried out on semi-fine wool.

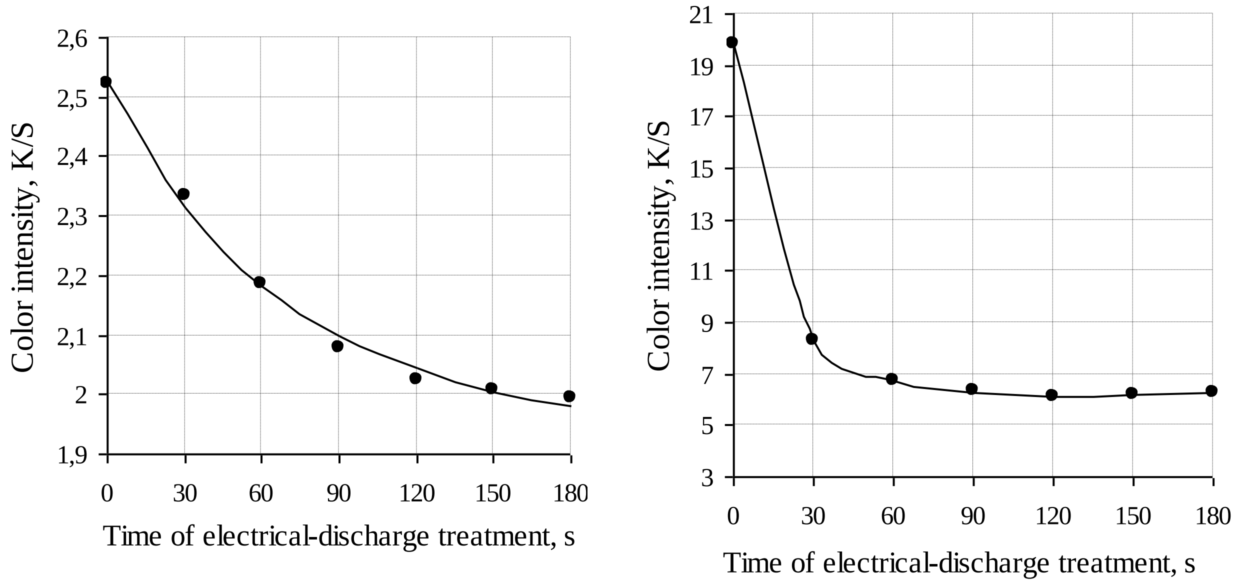


a) b)

Fig. 3.13. Effect of the duration of electrical-discharge treatment on the solubility of coarse wool fiber in chemical reagents:

a) NaOH: $y = 2{,}959 + 0{,}698 \cdot \cos(0{,}014x + 0{,}617)$, $S = 0{,}0785$, $r = 0{,}9938$;

b) UHR: $y = 1{,}324 + 0{,}418 \cdot \cos(0{,}017x + -0{,}064)$, $S = 0{,}0350$, $r = 0{,}9974$.



a) b)

Fig. 3.14. Effect of the duration of the electrical-discharge treatment on the dyeability of coarse wool fiber by specific dyes:

a) Diazol scarlet R: $y = \dfrac{1{,}918}{1 - 0{,}241e^{0{,}011x}}$, $S = 0{,}0160$, $r = 0{,}9978$;

b) Basic methylene blue: $y = \dfrac{19{,}850 + 0{,}387x}{1 + 0{,}097x - 0{,}0001x^2}$, $S = 0{,}0734$, $r = 0{,}9999$.

The results of dyeing with specific dyes (Figure 3.14), indicating a decrease in the intensity of the resulting stains with an increase in the time of electrical-discharge treatment, confirm the integrity of the cuticle and cortex of wool. It should be noted that in the case of dyeing with diazol scarlet R an insignificant change in the value of the K/S function is observed after 120 s of exposure to EDNBC, and in the case of dyeing with methylene blue an insignificant change is observed after 60 s. Thus, it can be concluded that the compaction of the surface of coarse wool occurs in a shorter treatment time compared to the semi-fine wool.

Complex analysis of the results of the investigation of the effect of the duration of the action of EDNBC on the basic quality indicators of coarse wool fiber allows us to conclude that the necessary modification effect, which ensures the maximum increase in whiteness and strength, is achieved already in 120 seconds of treatment.

In Table 3.3 shows the results of the change in the physical, mechanical, chemical and technological properties of coarse wool fiber before and after the electrical-discharge treatment for 120 seconds.

Table 3.3

Change in physical, mechanical, chemical and technological properties of modified coarse wool fiber

Parameter		Fiber			
		unpigmented		pigmented	
		untreated	modified	untreated	modified
Whiteness, %		39,3	43	10,8	11
Relative breaking load, cN/tex		9,28	9,33	8,16	8,22
Solubility in technological solutions, %	NaOH	3,5	2,26	3,55	2,30
	UHR	1,75	0,9	1,07	0,58
Intensity of coloring with specific dyes, K/S	Diazol scarlet R	2,521	1,993	–	–
	Basic methylene blue	19,85	6,281	–	–

Continuation of Table 3.3

Average fineness, µm	36,1	34,3	31,5	29,6
Crimp, %	3,30	7,56	11,11	15,66
Degree of felting, g/cm^3	0,185	0,171	0,194	0,180

Thus, on the basis of a complex analysis of the results of the study (Tables 3.2, 3.3) the effects of the duration of the action of EDNBC on the physical, mechanical and chemical properties of wool of different fineness, it is established that the optimum time of preliminary electrical-discharge treatment, which ensures the maximum increase in whiteness and strength, is 180 s for semi-fine wool and 120 s for coarse wool.

CONCLUSIONS TO SECTION 3

1. Based on a theoretical study of the processes occurring during the electrical-discharge treatment, it has been suggested that the complex effect of the electrohydraulic shock and water breaking products will allow for the preliminary modification of the wool fiber during its bleaching in order to improve its technological and operational properties.
2. It has been established that the redox potential of the working medium is reduced from 58 to 46 mV for 180 s with electrical-discharge treatment. And the tendency to decrease the redox potential persists after the cessation of exposure. Therefore, the chemical processes occurring during the electrical-discharge treatment of the fiber will be predominantly of a restorative nature.
3. A mechanism for the modification of wool fibers in the process of its preliminary electrical-discharge treatment is proposed. The proposed mechanism is due to the simultaneous action of electrohydraulic shock and active particles arising during the breaking of water, which consists in the reduction and reoxidation of disulfide bonds of keratin of wool. The formation of new covalent bonds between the polypeptide chains leads to an increase in strength, an increase in resistance to hydrolysis, as well as a decrease in the felting of wool fibers during processing and operation of finished products.

4. As a result of the study of the effect of electrical-discharge treatment on the surface of wool fiber with the help of the Allwörden reaction, it is established that EDNBC has a direct effect on the hydrophobic lipid layer of the epicuticle, without affecting the deeper layers of the substrate, which agrees with the results obtained by dyeing with specific dyes. Preservation of the main part of the cuticle of the modified fiber will provide high strength characteristics of bleached wool.

5. Complex analysis of the results of the investigation of the effect of the duration of the action of EDNBC on the physical and mechanical (whiteness, relative breaking load), chemical (solubility in alkali and urea-hydrosulphite reagent, coloring by specific dyes) and technological (fineness, crimp, felting) properties of wool allows us to conclude that the optimum time of preliminary electrical-discharge treatment for semi-fine wool fiber is 180 seconds and for coarse wool is 120 seconds.

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CONTENTS

Scientific publication

Saribyekova Yu.G., Asaulyuk T.S., Semeshko O.Ya.

PREPARING OF WOOL FIBERS FOR THE PRODUCTION OF HIGH-QUALITY FABRICS AND KNITWEAR

Monograph