ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 1, pp. 193–204. © Pleiades Publishing, Ltd., 2013.
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Nanosized Compounds in Textile Materials Finishing Processes

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Received July 21, 2011

Abstract—Application possibilities of nanosized agents in finishing of textile materials of different fibrous structure are considered. A new coloration technology based on the use of nanosized interferential pigments is presented.

DOI: 10.1134/S1070363213010404

For the last 10–15 years many countries with developed scientific and industrial potential have started active research and application of nanotechnologies in textile industry. The transition to new technologies is well-justified and has certain prerequisites.

Natural textile fibers of plant or animal origin are natural nanoporous materials with the size of pores within a range of 1–20 nm. It is for this reason that products based on such materials are characterized by high sanitary-hygienic and consumer properties [1, 2]. A special electro-spinning technology makes it possible to obtain ultrathin chemical fibers used for production of textiles for industrial and medical purposes [3]. Introduction of nanosized particles of the filler into the solution or melt of synthetic fiber-forming polymers makes it possible to obtain fibers (materials, products) with a high mechanical strength and electrical conductivity, having hydrophobic, oleophobic, and antimicrobial properties, sensitive to temperature fluctuations and to parameters characterizing conditions of the environment and the human body [4]. Such materials already find application in the sphere of provision for security bodies, sports, medical services, and textile production for household and special purposes. The most widely used filling materials are represented by various forms of carbon (including fullerenes), natural minerals, and oxides of metals (Ti, Mn, Zn, Sn etc.). Research works aimed to identify possibilities to introduce nanoparticles of different nature into the structure of fibers and polymer (in particular, textile) materials are carried out [5, 6].

A direction of activities applying nanoobjects and nanotechnologies in the processes of textile coloration (dyeing, printing) is in progress. It is well-justified as molecules or ions of dyestuffs, the size of which reaches only to 2–3 nm, are distributed on the surface of the material or penetrate into the structure of fibers, where their self-assembling into mono- and poly-adsorption layers not more than 3–6 nm thick takes place. In case of applying active dyes they form a strong (covalent) bond with functional groups of fibers [7]. Another direction raising certain scientific and future practical interest is connected with the formation of so-called textured colors on textile materials without using chromophoric compounds. The mechanism of creation of such colors is based on the interaction of light and nanostructural systems, which have pores of certain size and geometry (interference effects) [8]. This mechanism is implemented not only to produce color images but also to create the effect of invisibility of some object [9].

Another important area of application of nanosized compounds is the final finishing of textile materials aimed at improving consumer properties and obtaining new effects by attaching different container structures (nanocapsules, liposomes, macrocyclic compounds with nanosized hollows inside the cycle etc.). onto (or into) the fibrous substrate. Thus, it is possible to provide materials and products with hydrophobic and oleophobic properties, reduced flammability, biocide, therapeutic, and repellent properties, as well as to give the material a stable pleasant fragrance through capsulation of nanoparticles of odorants in the structure of the fibrous material etc. [10, 11].

For many types of textile materials the final finishing is the most important stage of the general chemical technology, as this stage determines the quality, comfort, and special properties of the end product. In this process an important role is played by agents, possessing the properties of softeners, as well as by the operation of finishing of textile materials using this type of agents. As a rule, at this stage there is a combination of chemical and mechanical processes of textile materials treatment [12].

It is quite common to combine the application of softeners with agents of other purpose, more specifically with crosslinking agents (for flax), antifelting agents (for wool), antipyrens, antistatic agents, and hydro-oleophobic agents. In this case, simultaneously with the softening effect it is possible to increase elasticity of the material, improve its washing ability, give hydrophobic and oleophobic properties to the treated materials [13]. The softening finish facilitates cutting of fabrics, provides synthetic materials with natural handle close to natural fibers, and increases the degree of comfort of the end products.

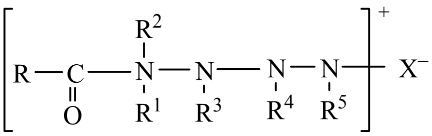
In terms of chemical composition, softening agents applied for textile finishing are ionic (anionic, cationic, and amphoteric) and non-ionic compounds. A significant part of the agents are represented by derivatives of organosilicon compounds [14].

A number of amine derivatives possess the properties of cation-type softeners. Such products are listed below.

Salts of tertiary amines $RNR^1R^2 \cdot HX$, where R = alkyl, X = acetate or glycol-acetate group. These agents are used as emulsifiers, wetting agents, and textile auxiliaries in the process of cotton fabrics boiling.

Quaternary ammonium compounds $[RNR^1R^2R^3]X$, where R = alkyl, X = Hal, SO_3H. Application of salts of quaternary ammonium bases is difficult due to their increased resistance to biodegradation (complexity of degradation in waste waters).

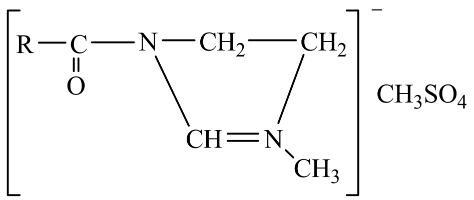
Salts of amidoamines



$$\left[R-\underset{\substack{\|\\O}}{C}-\underset{R^1}{\overset{R^2}{N}}-\underset{R^3}{N}-\underset{R^4}{N}-\underset{R^5}{N}-\right]^+ X^-$$

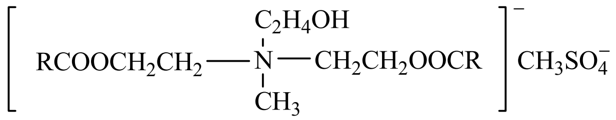
where R = H, alkyl, X = acetate or glycol-acetate group. They are represented by compounds based on a combination of stearic and palmitic acids [15, 16]. The higher is the degree of hydrogenation of fatty acids, the more evident is the textile material softening effect; moreover, the material displays no yellowing after curing.

Salts of imidazolines



Salts of aminoesters $RCOOR^1NR^2R^3R^4X$, where R = alkyl, hydroxyalkyl, X = Cl, CH_3SO_4 etc.

The typical structure of this group of compounds looks as follows:



$$\left[RCOOCH_2CH_2-\underset{CH_3}{\overset{C_2H_4OH}{N}}-CH_2CH_2OOCR\right]^- CH_3SO_4^-$$

The degree of solubility, wetting ability, and softening degree ambiguously depend on the length of hydrocarbon radical [17].

Anionic softeners $M^+RSO_3^-$ or $M^+ROSO_3^-$ (where R = alkyl, aryl, M = Na, K) are rarely used directly as softening agents (with the exception of propylene derivatives). Most frequently they act as anionic surfactants.

Non-ionic softeners $R(OC_2H_4)_nOH$ or $R(C_2H_4)_nOOH$ (where R = alkyl) are represented by different types of compounds, including fatty alcohols and their ethoxylated derivatives, ethoxylated fatty amides, amines, paraffins etc. [18], which are capable of formation of stable dispersion systems in the presence of emulsifiers. In order to increase solubility of non-ionic softeners they are applied in combination with cationic products; in such conditions there are cases of synergistic effect [19].

Silicones. The most widely applied softening agents in textile and light industries are based on organosilicon polymers – silicones [20]. This group of softeners is principally different from the above-listed low-molecular compounds of ionic and non-ionic character. The possibility to use these products in a number of textile materials finishing operations is related to the specific character of silicone structures and, correspondingly, properties of these polymers.

Thus, a chain of polyorganosiloxanes is based on Si–O–Si bonds with side organic radicals (analogous to C–O–C bond in natural high-molecular substances). Due to high energy and the mobility of Si–O–Si bonds silicones have a low melting temperature of crystalline forms, reduced glass transition temperature, relatively low viscosity of emulsions (the size of dispersion phase droplets in silicone nanoemulsions amounts to 40–60 nm at average), low values of the viscosity temperature coefficient, low surface tension degree, and friction coefficient [21]. A wide range of application of organosilicon agents includes their usage as softeners and hydrophobic agents in textile industry [22].

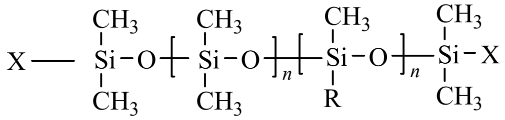
The specific character of silicones properties is related to simultaneous presence of inorganic and organic bonds (Si–O, H–Si–O, Si–CH_3 CH_3–Si–R) in the macromolecule. The former are of partially ionic nature, and taking into account lower electropositivity of the silicon atom side methyl groups are more tightly bound to the main chain as compared to other organic molecules [23]. Thus, the considered silicone agents combine so-called silicone and oil softening effects, which increases the efficiency of their application in general. Therefore, in the course of directed synthesis of organosilicon softening agents it is reasonable to introduce additional organogenic elements (N, S etc.) into their structure. Aminoorganosilicon polymers with repeated side methyl radicals can serve as an example. The specific property of such polymers is a high mobility of chains with free rotation of –Si–O-groups ($E_{\mathrm{rot}} \approx 0$ kJ mol^{-1}), elasticity, high value of the films slip factor, low surface tension (20–22 mN/m), and cohesive-adhesive characteristics as compared to the fibrous substrate. Treatment of textile materials with aminoorganosilicon nanoemulsions preserves the texture of the materials and provide them with water-, oil-, and soil-resistant properties [24]. The mechanical strength of the applied films results from the high energy of –Si–O (445 kJ mol^{-1}) and –C–O (358 kJ mol^{-1}) bonds; at the same time, they are quite sensitive to high temperatures [25]. In connection with the low glass transition temperature elasticity of the films is preserved within a temperature range of 90–200°C without significant changes in the physical characteristics.

Silicone film coatings are chemically inert; they are sensitive only to the effect of strong oxidizing agents and concentrated alkali solutions at increased temperatures. Exposure to UV radiation for a sufficiently long period of time has a degrading effect [26]. Silicone films on the surface of textile materials increase the modulus of elasticity of the fiber, yarn, or fabric. Air diffusion (of nitrogen and oxygen) through such films is not hindered; thus, treated materials and products maintain high air permeability and possess good sanitary-hygienic properties [27].

Polydimethylsiloxanes $[(CH_3)_2\,SiO]_n$

Polydimethylsiloxanes are one of the first groups of organosilicon softeners applied for finishing of textile materials. The ability to form cross links at ⩾Si–OH and ⩾Si–OR groups ensures high stability of the finishing effect. Apart from softening, agents of this group have demonstrated good results in terms of increasing strength degree of colors and resistance to the effects of “cutting-trough” the material at high-speed sewing machines [28].

Aminosilicones



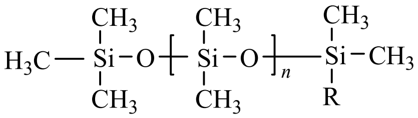
$$X-\underset{CH_3}{\overset{CH_3}{Si}}-O-\Big[\underset{CH_3}{\overset{CH_3}{Si}}-O\Big]_n\Big[\underset{R}{\overset{CH_3}{Si}}-O\Big]_n-\underset{CH_3}{\overset{CH_3}{Si}}-X$$

where R = $(n\text{-}C_3H_7)NH_2$ or $(n\text{-}C_3H_7)NHCH_2CH_2NH_2$.

This type of textile auxiliaries dominates over softening agents for textile materials; it ensures a high level of special types of finishing (Megasoft, Supersoft).

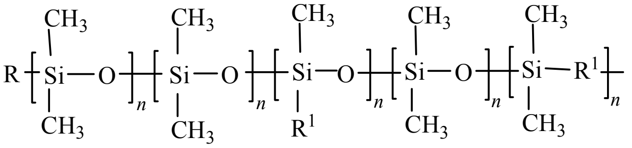
The softening effect can be regulated by changing a number of functional groups and molecular weight (viscosity) of the polymer; distribution of substituted amino groups in the chain; nature of end groups X, capable (X = OH, OR) and not capable (X = CH_3) of crosslinking reactions [29]. The number of amino groups in the main chain of the polymer determines affinity of the agent to fibers of different nature, their degree of yellowing, and hydrophobic behavior of the treated material [30]. The process of film-formation and cross-linking of macromolecules goes slowly due to the low speed of formation of intermolecular bonds; it can be accelerated by applying special catalytic additives (for example, oligomers with OR-groups) [31].

Investigation of the interconnection between the softening effect and the wetting ability of the fibrous material, on the one hand, and the chemical structure of organosilicon compounds, the size of emulsion droplets, and characteristics of the structure and fiber composition of the textile material, on the other hand, make it possible to identify the patterns for silicone polymers of the following structure:



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{R}{Si}}-CH_3$$

where R = $(CH_2)_3NH(CH_2)_2NH_2$.



$$R\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{R^1}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{CH_3}{Si}}-R^1\right]_n$$

where R = OH, OCH_3, CH_3; $R^1 = (CH_2)_3NH(CH_2)_2NH_2$.

Aminosilicones form highly-oriented films with even distribution on the substrate due to dipole-dipole interaction, formation of hydrogen bonds, and demonstration of electrostatic forces, which is most apparent in case of finishing of cellulose-containing materials.

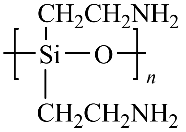
Dimethylsiloxanes $[(CH_3)_2SiO]_n$ are characterized by a low softening effect and wetting ability in relation to textile materials. It is related to non-uniformity of the formed film and its weak interaction with the fibrous substrate.

Epoxy silicones

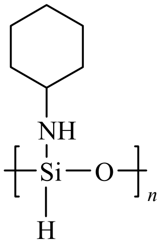
$$\left[Si(CH_3)-O\right]_n\left[Si(CH_3)(OCH_2CH_2)-O\right]_m Si(CH_3)-OH$$

Epoxy silicones produce a hydrophobization effect and possess a higher softening ability due to the demonstration of polar interaction forces between the finishing film and the fiber.

Aminoethyl–Aminopropyl–Silicones and Cyclohexylamino–Silicones



$$\left[\overset{CH_2CH_2NH_2}{\underset{CH_2CH_2NH_2}{Si}}-O\right]_n$$



Aminoethyl-aminopropyl-silicones and cyclohexylamino-silicones produce an identical softening effect. Nevertheless, preference is given to aminoethyl-aminopropyl-silicones as their influence is more effective, which is attributable to the steric proximity of two NH_2-groups. In general, silicone agents with primary amino groups produce a better softening effect as compared to secondary amino groups [32].

Silicones are poorly soluble in water and agents developed on their basis are applied in the form of emulsions. The average size of silicone emulsion dispersion phase particles and the character of the dispersion phase distribution according to the particle size depend on the ratio between the organic phase of the emulsion and the emulsifier, which can vary in a wide range from 8:1 to 1:1 [33].

It should be noted that nanoemulsions can be obtained only using organosilicon compounds, containing amino or substituted amino groups with the mass fraction of silicone ranging from 5 to 85% [34]. Distribution of the emulsion and films on its basis on the textile substrate depends on the size of particles; as a rule, microemulsions are precipitated on the surface of fibers and filaments, while nanoemulsions penetrate into interfiber spaces at significant depths (correspondingly, the effects of surface and internal softening manifest themselves [35]).

Comparative studies of a large number of silicone emulsions make it possible to find out that the softening effect is determined by the orientation and character of the agent distribution on the surface of the fibers and depends on the strength of bonds established between them [36]. The softening effect is also influenced by the dispersion degree of particles and the viscosity of emulsions, which determine their wetting ability. Selection of the silicone agent, in particular, amine polymer is made taking into account the content of amino groups in it, more specifically the content of amino groups which ensures the maximum softening effect correlates with the type of the textile material under treatment. For example, the agent for cotton textile and knitted fabrics should have a much higher content of amino groups as compared to cotton-polyester materials; and the maximal content is required for textile materials made of hydrophobic synthetic (polyester) fibers [37]. With an increase in the number of NH_2-groups and reactive radicals in general there is an increase in softness and hydrophobic behavior of the textile material finished with the use of nanosilicone emulsions.

Softeners based on nanosized aminosilicones are characterized by duality of properties: the main organosilicon chain gives them hydrophobic properties, while the presence of amino groups capable of protonizatio confers hydrophility. For this reason, such agents can get sufficiently securely fastened both on hydrophobic (synthetic) and hydrophilic (natural) fibrous materials [38]. Possible options of such interactions are presented in the figure.

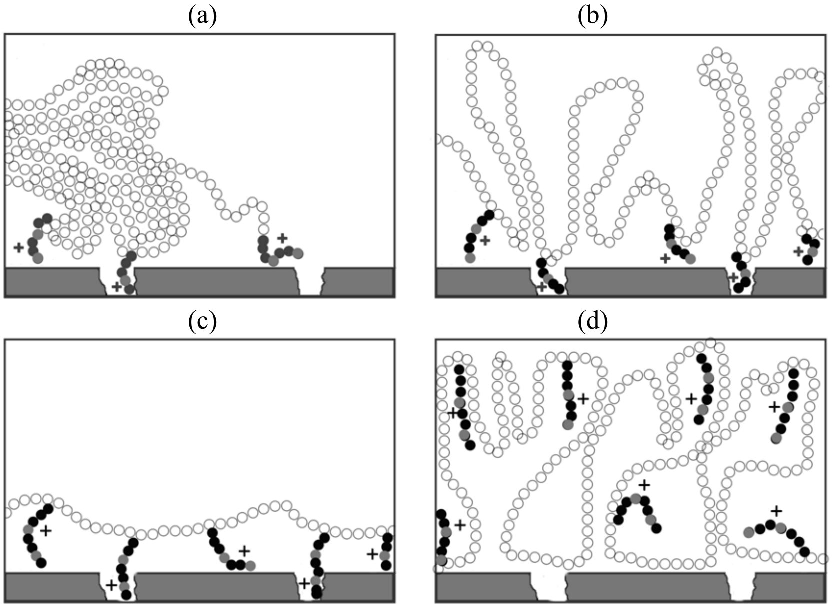


Fig. 1. Scheme illustrating aminoethyl–aminopropyl–silicone interaction with cellulosic fiber and formation of cellulosic coating: (a) uneven coating, low softness level; (b) optimal number of protonated NH_2-groups, high softening and hydrophobic effects; (c) even coating, absence of softening effect with preservation of hydrophobic properties; (d) excessive number of protonated NH_2-groups, high softening effect.

The effects of softening, elasticity, reduced friction factor, and correlations of the degree of hydrophilic and hydrophobic properties of the coating depend on the structure of the aminosilicone nanosized agent and the nature of the fibrous material. A significant impact on these properties is made by temperature conditions of the technological processes of drying and thermal treatment of the finished textile material.

Let us turn attention to the specific features of the effect of nanosized softeners.

A significant number of works is dedicated to studies of the softening mechanism [39–42]; however, it is not fully clarified yet. Molecules of the majority of compounds used as softening agents have a diphilic structure; they contain long hydrophobic hydrocarbon radicals (up to 18 atoms of carbon) with hydrophilic groups adjacent to them, like molecules of surface-active agents; however, unlike the latter, softeners are poorly soluble in water and form non-transparent dispersions of a micellar structure. Nanosized softeners of such composition are inclined to form micelles of complicated spherical bubble-type structure with inclusions of the aqueous phase.

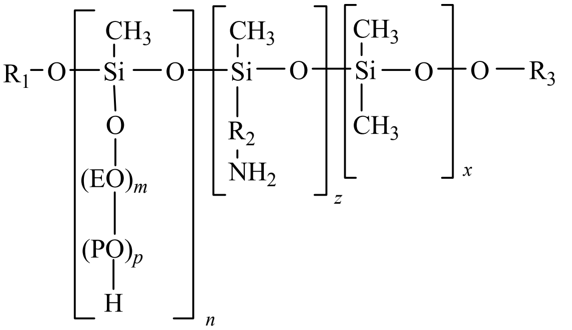
Cation-type softening agents interact with fibers having a negative charge on the surface (cellulose, polyacrylonitrile, polyester etc.), forming ionic bonds with the positively-charged cation or micelle at orientation of hydrophobic areas, ensuring antifrictional and softening effects. Polymolecular sorption of the softener on the surface of the fibers is considered more probable; however, multilayer structures are more sensitive to mechanical stresses and factors of operation of textile materials and products [43]. An increase in length of hydrocarbon radicals in macromolecules of softening agents increases a possibility of their interaction with the fibrous substrate and contributes to the strengthening of the bonds with them [44].

In principle the considered softening mechanism also covers micro- and macrostructural softening agents of different chemical nature, capable of forming multilayer coatings on the surface of textile materials (polyolefins, anionic and amphoteric compounds, organosilicon emulsions etc.) [45].

Application of traditional silicone softeners usually leads to a reduction in the wetting ability of the textile material (hydrophobization), which in some cases breaks the requirements set for certain types of products. This effect of silicone softeners can be eliminated if positively-charged tertiary $[–N^{+}H(R)_2]$ or quaternary $Z–N^{+}(R_2)X$ ammonium groups are introduced into the macromolecule (in the middle or at the ends of the main polymer chain). Another possibility is to combine silicone softeners with hydrophilic polymers (polyethylene- or polypropyleneglycols, polyvinyl alcohol, polyvinylpyrrolidone etc.) [46].

Emulsions of softening agents are applied on textile materials using padding machines, jet finishing machines, and circulation-type machines. During this process the agents are subjected to significant shearing deformation effects, which can cause their destabilization and degradation. In general, nanosized emulsions are more resistant to shearing deformations than coarse dispersion systems and less prone to sedimentation of particles, which correspondingly reduces unevenness of softening. Nanoemulsions based on aminoglycol-silicones are the most stable; however, in this case only average softening degree can be achieved [47]. Moreover, nanosized emulsions are not sensitive to changes of pH of the environment. It is also important that a possibility of their adherence onto the squeeze rollers is eliminated; contamination of the processed material. The specific feature of the structure of aminoorganosilicon polymers contributes to self-emulsification of particles, as a result of which the emulsion achieves ultra-high stability under conditions of storage and implementation of the technological process. As a consequence of self-emulsification the sizes of particles go down (below 100 nm) and from microemulsion the system turns into nanoemulsion.

In the process of emulsification of the organosilicon polymer, containing NH_2-groups, in the presence of surface-active agents a hydrophilic silicone nanoemulsion is formed



$$R_1-O-\left[\overset{CH_3}{\underset{O-(EO)_m-(PO)_p-H}{Si}}-O\right]_n-\left[\overset{CH_3}{\underset{R_2-NH_2}{Si}}-O\right]_z-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x-O-R_3$$

where EO are ethoxylated groups, PO are propoxylated groups.

In the structure of the specified compound hydrophilic ethoxylated groups are introduced directly into the chain, which contributes to its intensive self-emulsification. Treatment of the textile material with such agent provides the material with soft handle, elasticity, hydrophobic and soil-resistant properties.

A distinguishing feature of nanosized textile auxiliaries is hydrophilization of hydrophobic surfaces, for example, polyester fabrics. As a result, there is an increase in the degree of hygroscopicity and sorption capacity of the substrate, which contributes to intensification of its colorability in the processes of coloration and printing. As a rule, the effect of such agents has a complex character, i.e. in case of single finishing of the material it is possible to obtain several finishing effects in accordance with the end products functionality.

Using special emulsifiers (polyglycol surface-active agents) it is possible to prevent negative consequences of application of silicone emulsions, which manifest themselves in thermomigration of disperse dyes on polyester materials with a reduction in the resistance of the colors to friction.

It is known that the efficiency of nanosized agents is related to the specific properties of coatings formed on the surface of the polymer substrate [48, 49]. St. Petersburg Institute of Technology and Design performed a series of studies demonstrating increased efficiency of application of nanosized emulsions and colorants in the processes of printing and final finishing of textile materials. Traditional macro- and microemulsions and nanoemulsions based on amino-organosilicon and fluorocarbon copolymers were used in the experiments (Table 1). It was demonstrated that finishing of fibrous materials from natural and synthetic fibers using hydrophilic nanoemulsions significantly increased hygroscopic properties and moisture content of the material. It is possible to suggest that this effect is caused by the specific character of the process of self-assembling of hyper-branched structures with the formation of ultrathin and dense films on the surface of the substrate, as well as by the presence of fluorine atoms and hydrophilic groups [COOH, OH, NHR, $(CH_2CH_2O)_n$ etc.], having definite orientation at the phase separation border, in the composition of copolymers. As a consequence of hydrophilization of the fiber surface it is possible to expect an increase in the values of intensity and strength of colors, in particular, obtained as a result of coloration and printing of hydrophobic polyester fabrics with disperse dyes [50]. It is indirectly

Table 1. Effects of textile materials treatment with finishing emulsions

Name of agent	Agent composition and form of application	Achieved finishing effect	Manufacturer
Rucoguard AIR	Emulsion based on perfluorinated acrylic compounds	Water- and soil-resistant properties	Rudolf-Chemie
HPC	Fluoroorganic emulsion	Water-, oil- and soil-resistant properties	3M Company
Pluvoperl GR	Fluorocarbon resin emulsion	The same	CHT
FCY	Fluoroacrylate	Water-, oil- and soil-resistant properties	HCH
Nuva TTC	Emulsion of fluorinated copolymers	Hydro- and oleophobic finish	Clariant
Microcill IDRO	Hydrophilic aminoorganosilicon nanoemulsion	Complex effect	Prochimica Group
Rucostar E^3	Fluorocarbon emulsion with nanosized particles (20—90 nm)	The same	Rudolf-Chemie

confirmed by an increase in the diffusion coefficient of disperse dyes in the polyester fiber after its treatment with nanosized agents Microcill IDRO and Rucostar E^3 (Table 2).

A possibility to achieve a high quality patterned color simultaneously providing the material with a complex of special properties is demonstrated by an example of preliminary finishing of furniture fabric from polyester fiber using micro- and nanoemulsions followed by the process of sublimation printing [51, 52]. It is found experimentally that a combined technology of finishing and heat transfer printing makes it possible to increase hydrophobic and oleophobic properties, as well as soil- and crease-resistance of the furniture fabric with a reduction in the handle rigidity. There is a simultaneous increase in fire-resistance of the furniture upholstery and a decrease in its static properties (Table 3) under conditions of applying additional nanoemulsion-based antistatic agent (Tetramon S) and antipyrens (phosphoric acid, carbamide, or Pirofix) into the finishing agent.

Tetramon S (3–4 g l^{-1}) makes it possible to reduce electrical resistivity on the surface of polyester fabric from 10^{14} to 10^8–10^{10} Ohm as a result of hydrophilization of the substrate surface and the formation of a thin and smooth film of the nanoagent on it, which leads to a decrease in the friction factor and contributes to weakening of the triboelectric effect. Antipyrens in the composition of nanoemulsions increase fire-resistance of the synthetic furniture upholstery due to the demonstration of P–N-effect (stable finishing effect; if the composition of the agent includes phosphorus or nitrogen alone, the finish is not wash-resistant) and due to the extraction of gases, not supporting combustion (CO_2, NH_3 etc.). High fire-resistance resulting from firm adherence of Pirofix agent ($[O{=}P(OR)_2CH_2\cdot\ CH_2NHCH_2OH]$) onto the polyester substrate in combination with a nanocoating, containing active hydrophilic groups, is registered [53, 54].

Significant advantages of applying hydrophilic nanoemulsions are primarily related to the size of the dispersion phase particles, which is 10–15 times smaller as compared to traditional finishing agents and amounts to 80–110 nm. It is found on the basis of the optical method (recording instrument Nanotrec, United States) that there is a dependence between the size of emulsion droplets and their aggregative stability. This dependence is close to inverse linear relationship, which testifies to the high stability of nanoemulsions (phase separation rate does not exceed 5–10% within 24 h).

The formation of thin homogeneous nanofilms on the fibrous material reduces its rigidity and increases the mechanical strength with significant adhesion to the substrate [55].

Table 2. Coefficient of diffusion of disperse dyes in polyester fiber

Fiber treatment mode	Diffusion coefficient, $D\times10^{10}$, $cm^2\ s^{-1}$	
	disperse yellow Z	disperse red 2S
Without preliminary treatment	5.33	6.18
Preliminary treatment with nanoemulsions		
Microcill IDRO	7.23	8.31
Rucostar E^3	8.42	9.80

Table 3. Degree of special properties of polyester furniture fabric

Property	Determination method	Property indicator	Average value	
			traditional technology	proposed combined technology
Water-resistance	Schopper method	Height of water column, mm	280	317
	Contact angle measurements	Contact angle, degree	107	130
Oil-resistance	Method of 3M Company	Absorption of heptane-oil mixture, conditional units	90	110
Soil-resistance	Photometric method	Degree of soot pollution, %	34	24
Crease-resistance	Measurements of crease recovery angle	Crease recovery angle, degree	165	185
Rigidity of fabric	Cantilever method	μN cm^2	8000	5400
Antistatic properties	State Standard GOST 19616-74	Surface resistivity, Ohm	Tanastat 6040 2.6×10^{11}	3.8×10^{14}
Fire-resistance of fabric	State Standard GOST 15898-70	Combustion period, s/length of charred section, mm	Pirofix (200 g l^{-1}) 26.7/0.8	7.0 /4.3

Table 4. Nanosized inorganic pigments

Type	Color	Particle size, μm	TiO_2 content, %	Density, g cm^{-3}	Bulk density, g/100 ml	Oil absorption, g/100g
KS100	Silvery pearl	10–60	29[a]	2.8–3.0	17–21	65–75
KS123	Shiny satin	5–25	39	3–3.1	23–27	65–80
KS153	Brilliant pearl	20–100	16	2.7–2.9	33–37	70–80
KS225	Blue pearl	10–60	52	3.1–3.3	40–44	55–65
KS235	Green pearl	10–60	57	3.2–3.4	49–54	45–55
KS249	Shimmering gold	10–100	26	2.8–3.1	40–44	55–65
KS259	Shimmering red	10–100	29	2.9–3.1	42–47	55–65
KS289	Shimmering blue	10–100	34	2.9–3.2	42–47	55–65

[a] Form of TiO_2 is anatase, other pigment is rutile.

Introduction of nanosized finishing emulsions into textile production makes it possible to create principally new promising finishing technologies, to expand the range, and to improve the properties of the end products maintaining high resource-saving and environmental-safety characteristics of the technology.

Another sphere of application of nanosized agents in textile production is the development of a discharge printing technology using nanosized inorganic pigments. Despite the dominating position of organic pigments, application of inorganic analogues retains its significance and has a tendency to further development. This fact is related to their water-, light-, and heat-resistance, high spreading capacity, and relatively low costs. Modern inorganic pigments are represented by artificially-produced finely-dispersed colored and achromatic salts insoluble in water and oxides of metals (Fe, Pb, Ti, Ba, Mg, Cr, Al, Zn, Co etc.) [56]. The following inorganic pigments are applied for printing of textile materials:

– white color pigments: titanium (TiO_2) and zinc (ZnO) white, barium sulfate, kaolin, aluminum hydroxides [$Al(OH)_3$], [$3Ba_8O_4 + 2Al(OH)_3$], and aerosil;

– yellow color pigments: chrome and iron-oxide pigments, and lead chrome;

Table 5. Assessment of influence of coloring agents Chemical composition on results of discharge printing using rongalit

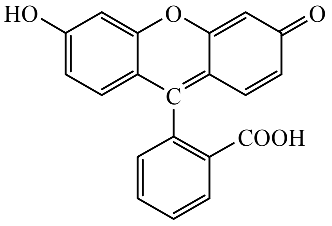
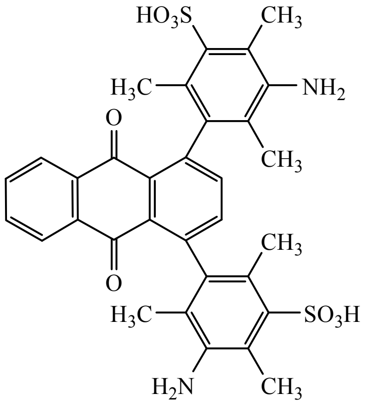
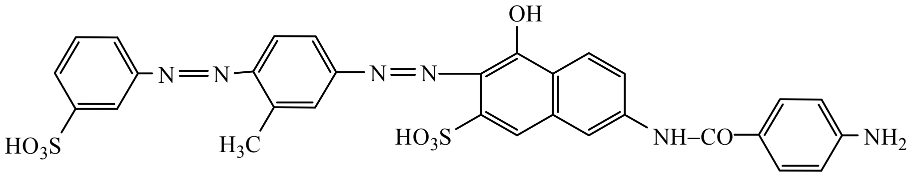
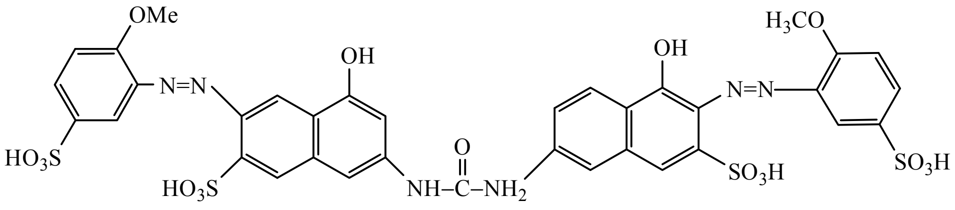
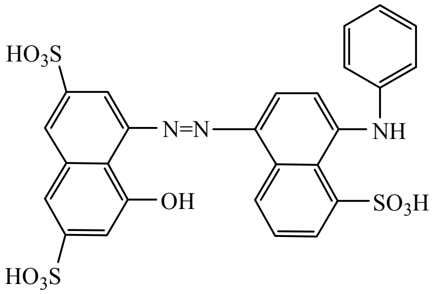
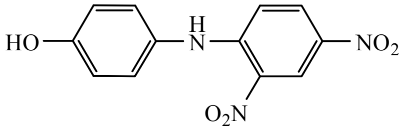
Name of coloring agent	Chemical composition of coloring agent	Discharging ability of color
Fluorescein (xanthene dye)		Not dischargeable, color changes are observed
Acid bright-blue anthraquinone		Low
Direct diazo-bordeaux S (diazo dye)		High
Direct ruby light-fast MU (diazo dye)		High
Acid blue 2K (monoazo dye)		Partially loses color
Disperse yellow fast 2K (nitro-dye)		No color changes due to application of discharge dyes

Table 6. Quality degree of discharge printing with application of nano-sized inorganic pigments

Background dye	Size of pigment particles, μm	Spreading of pattern outlines, mm	Color resistance to friction, points
Disperse violet K	KS-400, 10–60	0	4
Disperse yellow fast 2K		0	4
Disperse violet K	Gold 306, 10–60	0.05	4
Disperse yellow fast 2K		0	4
Disperse violet K	KS-100, 10–60	0	5
Disperse yellow fast 2K		0	5
Disperse violet K	KS-123, 5–25	0.05	5
Disperse yellow fast 2K		0.05	5
Disperse violet K	KS-153, 20–100	0.025	4
Disperse yellow fast 2K		0.075	4
Acid bright-blue		0	5
Direct turquoise light-fast		0	4
Direct ruby light-fast		0	4
Fluorescein		0	5
Acid blue-black		0	5
Acid blue 2K		0	5
Active bright-blue		0	5
Direct diazo-bordeaux S		0	4

– blue color pigments: milori cobalt complexes;

– golden, silver, and pearlescent powders (pastes); bronze and aluminum powders.

New generation inorganic pigments were applied within the framework of the present work (Table 4). Apart from that, a series of colored pearlescent pigments based on mica, titanium dioxide, and a mixture of inorganic and organic pigments (particle size of 10–60 and 20–100 μm) were used. The process of obtainment of interference pigments involves consecutive application of coatings formed by metal oxides with high and low refraction indexes on SiO_2 flakes through hydrolysis of the corresponding water-soluble metal compounds with the following separation, drying, and calcination of the formed product [57]. The particles of the obtained pigment are 2–5 μm long and 2–2000 μm wide; the length-to-thickness ratio is not less than 2:1. A semitransparent nanolayer of metal (or several metals) 20–200 nm (most commonly 60–120 nm) thick is applied on the mica base plate.

It is known that discharge printing is based on discoloration of the background color of the preliminarily dyed textile material. There are two major types of discharge printing: oxidation and reduction. The composition of discharge printing dyes includes the following reducing agents: sodium dithionite $Na_2S_2O_4$, rongalit (sodium formaldehyde sulfoxylate $NaHSO_2{\cdot}CH_2O$), and thiocarbamide dioxide (reducing agents AN) [58].

In the course of the experiment samples of textile materials (wool, polyamide, and cotton) were printed with dyes containing the specified reducing agents in accordance with the following formulation (g kg^{-1}):

reducer – 120
binder – 80
softener – 5
thickener – 20
water – to 1000

The efficiency of reducing agents was assessed on the basis of the color variation (ΔE) of the background and the discharge print. The obtained results (Table 5) indicate to high reducing ability of diazo dyes in case of rongalit application.

The following stage of research was dedicated to assessment of influence of inorganic pigments particle size on quality degree of the discharge print. Nanosized pigments based on mica and metal oxides, forming structural (interference) colors: silver-white series – KS 100, 123, and 153; interference series – KS 249 and 289; and golden series – KS 300 and 365, were used.

The quality of the discharge print was evaluated based on the degree of sharpness of the pattern outline and resistance of the pigment color to dry and wet friction [59]. The obtained data are given in Table 6.

Analysis of these data demonstrates that application of nanosized inorganic pigments in the process of discharge printing of textile materials makes it possible to obtain well-defined patterns with original design and coloristic effects. The obtained colors are stable as compared to printing based on organic pigments.

Therefore, application of nanosized finishing emulsions and coloring agents creates an opportunity to switch to processes ensuring the modern level of coloristic decoration and comfort of textile materials and products.

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