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GREY FLAX. DELICATE TECHNOLOGIES OF PREPARATION AND COLOURING

SZARY LEN. TECHNOLOGIE PRZYGOTOWANIA I BARWIENIA

Abstract

Ecologically safe method of preparing textile materials containing natural unbleached linen fibre has been developed. The process includes short-period treatment of gray fabric in air plasma of glow discharge followed by washing in hot water. It allows to retain natural silver-grey colouring of flax and to provide high hydrophilic properties. New original methods of white and colour discharge printing on grey linen textile materials have been developed. Formation of figures occurs due to local destruction of the painted impurity of flax by means of specially selected oxidizing agents. It was established, that only direct and active dyes in printing could be combined with bleaching composition on the basis of hydrogen peroxide.

Keywords: grey linen, gray flax, air plasma of glow discharge, white discharge printing, colour discharge-printing, hydrogen peroxide

Streszczenie

Opracowano ekologicznie bezpieczną metodę przygotowania materiałów tekstylnych produkowanych na naturalnej osnowie lnianej. Proces rozpoczyna powietrzna obróbka materiału w polu elektrostatycznym, po której następuje płukanie w gorącej wodzie. Ponadto opracowano nową, oryginalną metodę bielenia, barwienia i drukowania płótna lnianego. Pozwala na to autorska kompozycja wybielacza, stworzonego na bazie nadtlenku wodoru.

Słowa kluczowe: szare płótno, szary len, bielenie, barwienie, nadtlenek wodoru

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The variety of fabrics and models from a flax amazes imagination. That is rough dense canvases, friable hopsack, and translucent batiste. Also uses of such fabrics are extremely various: from fire hoses and a reinforcing material for plastics to the most thin ajour underwear and surgical threads. The flax is a unique natural fiber possessing along ecological advantages and high fastness properties. Many features of flax such as durability, low electric resistance, comfort, and natural bacterial action are superior compared to cotton textile. Linen has a plain surface, which gives it an amazing silky shine. In general these properties are characteristic for materials, containing non-bleached linen fiber, its natural colour has a lot of shades from light silver-grey to dark brown. Such fabrics are getting the increasing popularity in the world market. At the same time the assortment of the materials, basically formed at the expense of variations of weaving structure of a cloth, is substantially limited, as coloration by any types of dyes owning to the imposing of a dye on a grey background of fabrics, does not give pure bright coloring. Carrying out a complete cycle of pre-treatment deprives linen its natural colouring, originality and appeal.

An aspiration to keep natural colour of a linen fiber and at the same time to get an interesting colour effect led the authors to work out essentially new technologies of preparation and decoration of linen grey fabrics. An effective and ecologically safe way of preparing the fabrics from severe flax is plasma-chemistry technology developed at the department of Chemistry and technology of fibre materials in Ivanovo State University of Chemistry and Technology, Russia. It possesses special "colour" appeal, because it allows a natural silver-grey colouring to flax, to provide high consumer properties of textile materials and practically to exclude the application of chemical reagents for technological needs.

The technology of preparation includes a short-term ($40 \div 60$ c) processing of a material in air plasma of glow discharge and then after-washing in hot water. It was established that severe fabrics treatment in a plasma results in the destruction of the substances, which are on the surface of a fibrous material (for linen fabrics it is in starch size) to gaseous substances, which are removed from the plasma zone by vacuum pumping. The degree of fettling of a material from a starched sizing material reaches $80 \div 90\%$, therefore it is $15 \div 20\%$ above classical desizing. And a capillarity index reaches the level of $100 \div 130$ mm/h; fabric durability properties are being improved.

The plasma-chemistry technology allows essentially reducing duration of a preparation process of greasy fabrics from grey flax due to the exclusion of such labor-consuming, material and powering intensive operations as a desizing and bisulphate boiling. It practically eliminates the application of chemical reactants for the technological needs. Preparation time is reduced from $1.5 \div 2$ hour to $15 \div 20$ minutes. And the main advantage of this method is to preserve a natural original beauty and durability of a fabric.

The main base for these technologies is a principle of the discharge printing. This process was well-known and widely used early for obtaining white or colour drawings on a dyed fabrics at the expense of destruction of a fabric background and fixing a dye from a printing past. However to use this approach it is necessary to carry out preliminary dyeing of a material by the dyes that are damaged under the action of a special reagent (mostly by reducing agents).

A peculiarity of a linen fiber structure having lignin in its structure, is that natural "gift" which gives the chance to exclude operation of preliminary dyeing a textile material and to use a natural background of a fabric for the creation of drawings on it. The idea, which seemed to be on a surface, was realized at last in the technologies of a white and colour discharge print. The main principle taken as a base for a white discharge print (or local bleaching), is the possibility of decolouring non-cellulose admixtures thus keeping the color of a severe flax by bleaching structures on the base of oxidizing agents.

While working out the technology there arose a question of selecting a bleaching agent and technological modes that provide stability of structures at the stage of preparation, printing and drying combined with high action efficiency under the conditions of a short-term steaming. Thus it was required to obtain a new colour effect with the preservation of non-bleached flax refinement.

Table 1

Compositions of printing pasts on the base of hydrogen peroxide (I) and benzolsulfachloramid sodium (II)

Structure	Concentration in structure, g/kg	
	I	II
Hydrogen peroxide (100%)	3 ÷ 35	–
Sodium silicate (*d* – 1,43)	50	–
Benzolsulfachloramid sodium	–	50 ÷ 300
Acetic acid (98%)	–	1 ÷ 5
Thickener (solvitoza C-5)	to 1000 g	to 1000 g

From all oxidizing agents being tested at the stage of searching only hydrogen peroxide and benzolsulfachloramid sodium (Chloramin B) are satisfactory for necessary requirements in the print. Peroxide printing pasts provide higher whiteness and tone contrast as compared with that printing past on the base of benzolsulfachloramid sodium compound. Besides, the results are defined both by initial pale colour and the material invoice and compositions of printing pasts, which are presented in tab. 1 and 2.

Table 2

Influence of a bleaching agent type on the maximum whiteness and tone contrast between drawing and a fabric background

Fabric, the article		052240	07114	411	07102	10252
Fibrous structure		Cotton: jute PETP 50:20:30	Flax	Flax	Flax	Flax:PA 92:8
Surface density g/m^2		103	200	150	200	280
Volume density g/sm^3		0.245	0.526	0.517	0.512	0.474
Thickness, mm		0.42	0.38	0.29	0.39	0.59
Initial pale, %		**44.1**	**35.5**	**30.7**	**30.1**	**24.7**
The maximum whiteness after print the past, %	I	82	73	75	70	68
	II	65	60	66	60	55
Tone contrast after print the past, %	I	1.86	2.06	2.44	2.33	2.75
	II	1.47	1.69	2.15	2.0	2.23

Similarly, to the processes of classical bleaching one of the basic technological stages of local bleaching is steaming during which there is a lignin discoloration (fading) and white print formation. The influence of a type of bleaching agents and time parameters of the process on a whiteness level in print contour has been studied (fig. 2). It is established that the time necessary for an achievement of a maximum whiteness for peroxide pasts, is 3 ÷ 5 minutes while leaving 40% of lignin. The application of chloramines B demands longer steaming (7 ÷ 11 minutes), but at the same time the effective lignin removal (to 60%) is not absolutely necessary for the achievement of a high whiteness, which is 8 ÷ 10% more lower, than with peroxide bleaching.

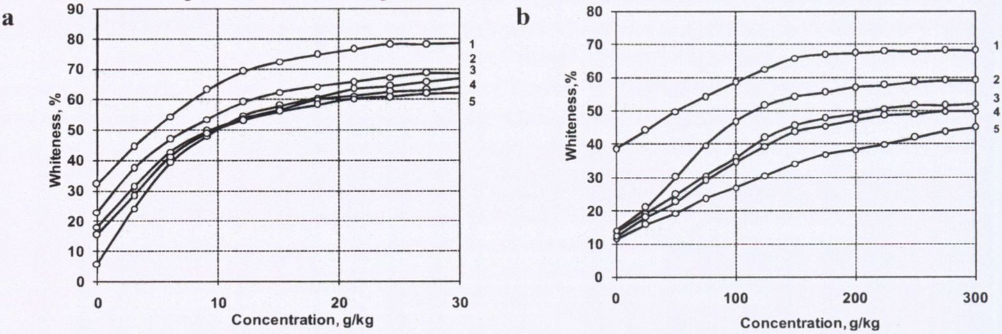
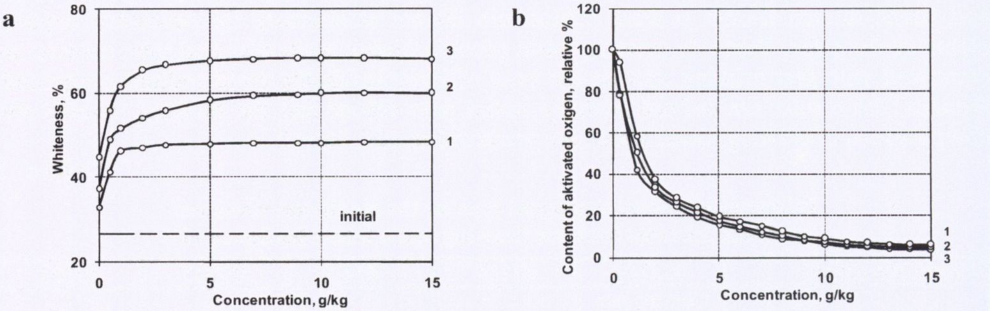


Fig. 1. Influence of bleaching agents concentration: hydrogen peroxide (a) and chloramine B (b) on a whiteness in print contour: 1 – art. 052240; 2 – art. 07114; 3 – art. 10252; 4 – art. 07102; 5 – № 411

Rys. 1. Wpływ koncentracji środków wybielających: nadtlenek wodoru (a) i chloramina B (b) na biel w obrysie wydruku: 1 – art. 052240; 2 – art. 07114; 3 – art. 10252; 4 – art. 07102; 5 – № 411



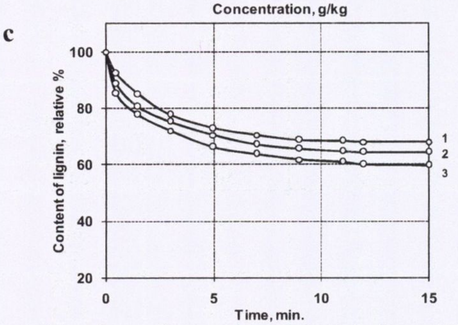


Fig. 2. Changes of a drawing whiteness (a), content active oxygen on a fabric (b) and content lignin (c) in process steaming after the process of printing with past H_2O_2; g/kg: 1 – 7; 2 – 20; 3 – 35

Rys. 2. Zmiany w bieli rysunku a), zawartości aktywnego tlenu na tkaninie (b) i zawartości ligniny (c) w procesie parowania po procesie drukowania pastą H_2O_2:, g/kg: 1 – 7, 2 – 20; 3 – 35

The data obtained make as believe, that the drawing whiteness is defined not only by lignin removal from a fiber, but also by the modification of its chromophore structures. It is confirmed by UV-spectra of lignin extracts in dioxane (Fig. 3). The basic process occurring in an alkali-peroxide environment of bleaching past I seems to be lignin hydrolytic destruction to the fragments removed during after-wash of a fabric.

As a result of the reactions occurring under the influence of past II, monomeric, oligomeric and the polymeric chlorinated agents of various structure can be formed in lignin, including o- and p-quinones. And the adsorption increase in the area λ ~250 ÷ 260 nanometer and "shoulder" occurrence at λ ~330 ÷ 340 nanometer confirm it.

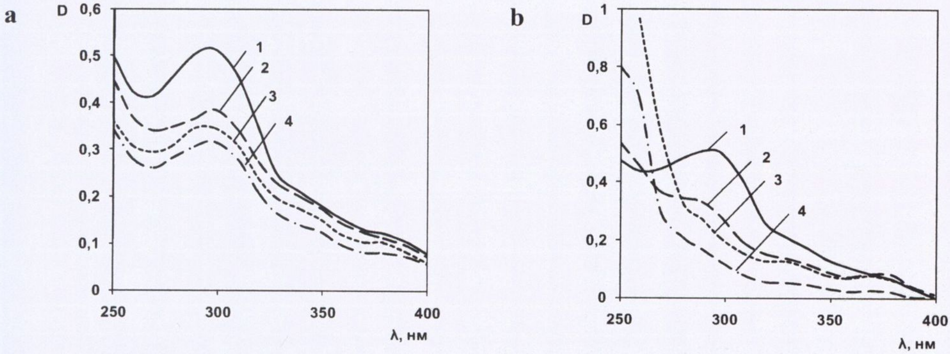


Fig. 3. UV-spectra of lignin dioxane extracts from a fabric printed with hydrogen peroxide (a) and benzolsulfachloramid sodium (b) pasts, their concentration respectively equals g/kg: 1 – an initial fabric; 2 – 30 (100); 3 – 6 (200); 4 – 90 (300)

Rys. 3. Widma UV ekstraktów dioxanowych ligniny materiału drukowanego pastami z nadtlenkiem wodoru (a) oraz benzolsulfachloramidem sodu (b), ich stężenie wynosi odpopwienio; g/kg: 1 – początkowa tkanina; 2 – 30 (100), 3 – 6 (200), 4 – 90 (300)

The effect of a discharge type of printing pasts is evident well by the quality of removal of other companions of a linen fiber – pectins, waxes, starch size (tab. 3).

Taking into consideration sufficiently enough concentrations of oxidizers applied during technology elaboration there could have been a high destruction of a fiber. However the loss, of the fastness properties and a cellulose fastness rating do not exceed 2 ÷ 5%.

The reason of such "delicate" action of the discharge printing pasts, are which do not effect a fiber short time of wet-heat processing and, in a greater degree of, a protective function of a printing structure containing a thickener, capable to perceive on itself a destruction of oxidizing action.

For the expansion of theoretical and technological colouristic prospects of research the methods for colour discharge printing were developed.

The absence of contradictions between these processes is a guarantee of successful use of coloured discharge printing.

The theoretical bases for coloured discharge are the combined ways of bleaching and dyeing of cotton fabrics. But great difference of colouring objects, concentration and time process parameters caused the search of some types of dyes and the definition of the conditions for their combining with bleaching printing composition.

Choice criteria were a stability of printing composition and bleaching properties of an oxidizing agent on one side – keeping a chromoform structure and colouring ability of dyes on the other side.

As a result of carrying out a complex of theoretical and practical research, and combining those results with the experimental data that cover more than seventy trade-marks of dyes, it was established that in the conditions of printing only direct and active dyes can be combined with bleaching composition on a base of hydrogen peroxide.

Table 3

Action of bleaching agents on linen fiber components

Fabric	№416		Art. 07114		Art. 10252	
	I	II	I	II	I	II
The residual maintenance of a starched sizing material:						
In a drawing contour	11	9	9	8	15	12
Against a fabric	94	51	92	52	95	49
Removal of an allied celluloses of a flax, %						
Pectins	75	63	76	68	80	75
Waxes	7	5	14	17	28	30
Degree of cellulose polymerization*	5480	5260	6230	6050	3150	2910
Cellulose damage rate	0.34	0.40	0.01	0.10	0.90	0.95

Structures I and II on a warp hydrogen peroxide and chloramine B respectively;
* – for greasy fabrics are equal 6360, 6240 and 4190 respectively.

The stability of hydrogen peroxide bath was studied by independent methods, namely, by gasometric and iodometric ones. On the basis of the results, a period of half-life and the rate constants of hydrogen peroxide decomposition reaction were calculated. These data as well as the results of the ability of dyes to be fixed on a fibre in the conditions of discharge printing evaluations allowed to divide all the dyes under research into three groups, i.e. incompatible, compatible in a limited with a peroxide bleaching agent.

Some other components of discharge bleaching composition (sodium silicate, thickener) influence a dye as well and it follows from the results of paper chromatographic mobility of a dye in the presence of sodium silicate and the presence along with a hyperchromic effect a batochromic decrease. Absorption maximum are reliable proofs of forming an eyeing compound possessing a greater molecular mass. It is logical to assume that the probability of appearing a sodium silicate-dye complex which a hypothetical model is given by Fig. 4. The latter has a considerable size and greater affinity to cellulose. It can be seen in the increase of an aye sorption by a fiber.

The absence of a negative influence of such complex on dye diffusion in a polymeric substrate was proved experimentally.

The colour characteristics of shades, their cleanliness and brightness are defined by stability and oxidizing ability of a bleaching agent in printing composition.

Having carried out series of experiments on fabrics of different types and clearness it was established that there exist optimum consent rations of an oxidizing agent in printing composition. Below this concentration owning to insufficient bleaching the colouring obtained are characterized by a low degree of cleanliness. The application of the concentrations above optimum causes an unproductive expenditure of a bleaching agent.

Qualitative bleaching in a drawing contour creates the conditions for an effective fixation of a synthetic dye, which content in a printing composition is defined by a required shade and coloring contrast of a drawing. By changing dyes and their concentrations it is possible to obtain colouring of wide color range, which are different in their intensity ranging from gentle pastel to dark saturated tones. The best colour effect of colour discharge printing is achieved at the maximum contrast between a gray background of a fabric and gentle pastel tones of a drawing.

Table 4

Compatibility of dyes with alkali-peroxide structure

Groups of Dyes	Direct	Reactive	Influence of a dye on hydrogen peroxide	Influence of alcalioxidising medium on a dye
Incompatible	Metalcontaining and wich have on there structure complex forming groups: symmetric ortoxyazogroups, groups of salicylic acid		Decompose catalytically. There appears foaming a printing composition	Is not fixed on a fiber. Can be bleached in printing composition
Arbitrarily compatible	Derivatives of 1amino-8oxy-3,6 (2,4) disulphoasid of naphthalene III (IV)		Do not influence	Change the shade during a long (more than 15 ÷ 20 mines) contact with hot alkaline solutions they are active in the short-term wet-thermal heatment (to 10 minutes).
Compatible	Azodyes, stilbene derivatives, 4,4'-diamino-benzanilide	Monochlortriazine, pirimidine and vinyl-sulphonye	Do not influence or increase to some extent the stability	A fixed well on a fiber
		Dihlortriazine		Are hydrolyzed, decrease the ability to be fixed.

a

b

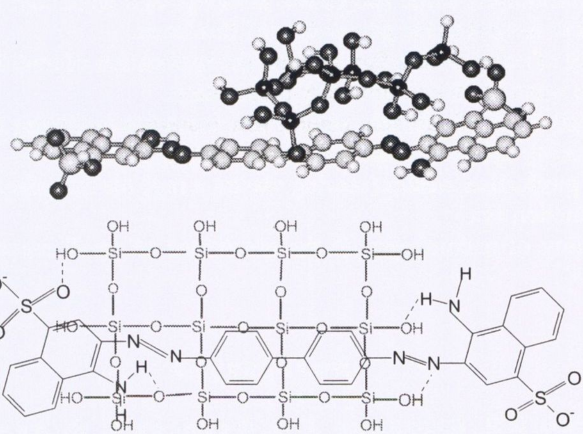


Fig. 4. Model of a complex structure; a – «sodium-dye silicate» complex,
b – the interaction of congo-red dye with sodium silicate

Rys. 4. Model kompleksowej struktury: a – kompleks sylikatu sodu,
b – interakcja barwnika czerwień Kongo z sylikatem sodu

A great advantage of the technology of colour corrosive press is the possibility of using direct dyes (which are practically not used in printing) and dichlortriasine active dyes which are easily hydrolyzed in an alkaline medium. The formation of a labile silicate complex with an active dye protects it from hydrolysis and gives the possibility to obtain qualitative colouring of light and mid-shades.

It is necessary to discuss one of the most important problems which arises in the process of development of this technology which requires a rather specific solution to, as it is known that when classical bleaching is carried out either by bath or a poor-steam process avoiding fabric drying the technology of a printing as a necessary stage includes intermediate drying the use of peroxide compositions is attended by the danger of a thermal bleaching agent decomposition. Possible solutions to this problem is potential exclusion from a stage of an intermediate drying for severe and low capillarity fabrics and to carry it out in mild conditions for hydrophilic materials, while print humidity are being set approximately to 30%. It will allow to keep peroxide bleaching activity and to provide an accurate drawing contour.

Taking into consideration the information given above this process of technological printing follows the simplified scheme: printing, drying if necessary, steaming and washing. The process can be carried out using typical and auxiliary equipments. In conclusion, the technologies of white and colour discharge press are developed which represent a new way of art-colouristic decoration of textile materials allowing enrichment and wide spread of various assortment of textile production in a linen industry.

Fig. 4 shows an example of decoration of the fabric from grey linen with the use of white and colour discharge printing.

The advantages of technological solutions are as following:

- The absence or minimum content (0.5 ÷ 2g/kg) of dyes in a printing composition gives an original properties and ecological advantages to natural flax.
- Production of semitone, white and colour drawings of a wide colour range that favorably show contrast to natural silver grey colour of flax linen.
- The possibility of using severe flax without the application of traditional labor consuming and expensive ways of then preliminary preparation.
- Greater and fuller use of valuable natural row materials including low-grade rough linen fiber for producing upholstery fabrics, textile wallpaper.
- The usage of production wastes (searing wastes a rag) for manufacture of clothes details, souvenir production etc.
- The applicability of technologies in the conditions of small manufacture as well as in industries.

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