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COMBINED DYEING TECHNOLOGY FOR FORMALDEHYDEFREE AND LOW-SHRINKABLE FINISHING OF LINEN AND SILK FABRICS

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Currently, there is a fashion trend related to designing garments made of linen, the so-called "environmental line". However, linen has a significant drawback - it is quickly crumpled and badly restores the original shape. For this reason, blended fabrics like linen-polyester are produced; content of the latter affects the preservation of the unique properties of flax. Flax is also treated with various latex based organosilicone preparations, which is a quite expensive technology.

It has been proposed in this paper to endow flax with low-wrinkle properties by means of modification with available and formaldehyde-free preparations based on polycarboxylic acids in the dyeing process, without changing fabric's composition.

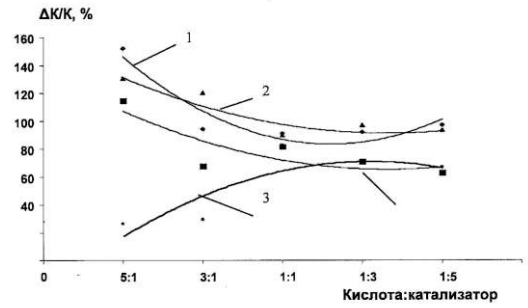
It is assumed that due to the presence of several groups, COOH acids can act as cross-linking bridges as a result of which internal structure of cellulose changes and represents no longer a linear structure, but is more a spatial three-dimensional structure which is resistant to external shrinking load. The nature and effect of catalyst concentration have been studied with the purpose to increase the effectiveness of "cross-linking" in the process.

Due to the set goal of combining two processes into one: - dyeing and final minimum-wrinkle finishing - in connection with high temperatures above 100^0C, heat-setting method is to be agreed upon. As catalysts, in most cases phosphorus salts and acids are referred to; in addition, studies have shown that inorganic salt with an acid reaction has sufficiently effective action. As the polycarboxylic acids, available and relatively cheap food acids were selected, containing –COOH and –OH groups in various combinations: dicarboxylic acid, dicarboxylic oxi-carboxylic acids, and tribasic carboxylic acid.

The process is carried out in a weak acidic medium, created both by acids and by catalysts. For this reason, preference is given to direct dyes which are relatively resistant to this kind of environment. The most stable dyes among the reactive dyes are the dyes which contain vinyl sulphonic group as active center.

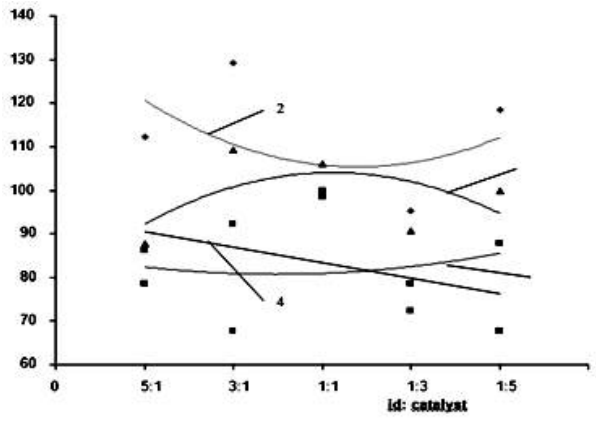
The results of dyeability (color yield) were evaluated by the dyeability reflection spectra by means of Gurevich-Kubelka-Munk factor in relation to a standard-sample dyed without the additives studied. Then, we constructed trend-dependent influence of the content of additives in the dye bath on various parameters (such as coloristic, mechanical ones - resistance to wrinkling, stiffness) in the form of polynomial curves of second order of mean square deviation from the experimental points.

Analysis of experimental data has demonstrated that practically in almost all cases introduction of these additives results in efficient increase of dyeability up to 120...160% (Picture 1).



Picture 1

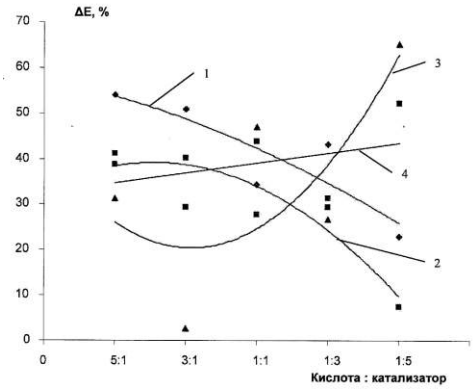
As mentioned earlier, polycarboxylic acid modifies cellulose with the formation of three-dimensional crosslinked structure, which is relatively resistant to wrinkling. It has been demonstrated that the maximum effect of low-wrinkleability increases this index to 120...130% (Picture 2).



Picture 2

As a rule, indicators of low-wrinkleability depend on the rigidity of linen cloth, which can contribute to either increase or decrease of the fold's opening angle.

Analysis of measurement results of linen samples' rigidity, dyed with direct and reactive dyes, has shown that there is no visible clear dependence between the sustainable opening angle of the crease and the rigidity (Picture 3). At the same time there is some effect of catalysts on these indicators, in such a case, it depends on the combination of nature of acid - catalyst systems.



Picture 3

It is known that change in the internal structure of fibers entails a change in its physical and mechanical properties, as it happens in standard treatment with N-methylol agents, and with the following reduction of strength of cellulose fibers. Study of breaking (rupture) characteristics showed an increase of strengthening by about 1.5 times.

Test results analysis of the stability of obtained dying to wet treatments showed strengthening of dying by 0.5 - 1 point, allowing to make assumption regarding a quite strong bond of dye with flax due to steric factor of three-dimensionality which holds the dye in the fiber structure.

It should be noted that the use of combinations of dibasic and tribasic acids provides a synergistic effect, while the increased rigidity of fabrics enables to increase resistance to wrinkling, which makes it possible to make an assumption about the "elasticity" of crosslinked three-dimensional supramolecular structure of cellulose, modified by polycarboxylic acids.

Metal cations have a significant impact on textile materials in the finishing process. It is known from the literature that they form complexes (which are different with regard to strength and structure) both with the dye, and with the fiber, that they affect the electrochemical properties of the fiber, structure and hardness of water. Metal ions can act as additional active sorption centers on the fiber. It is known that the interaction of metal with the dye in the dyeing process can lead to a change of coloristic parameters, fastness of dying and strength of the fiber itself.

One of the main problems in coloring of textile materials from protein fibers is the fastness of dyeing to wet treatments and to light, which is important for improving the quality of expensive natural silk, unique with regard to properties. In this regard, the task is set to use transition metal ions with the aim to strengthen both the dyeing and fibers, as well to improve coloristic characteristics.

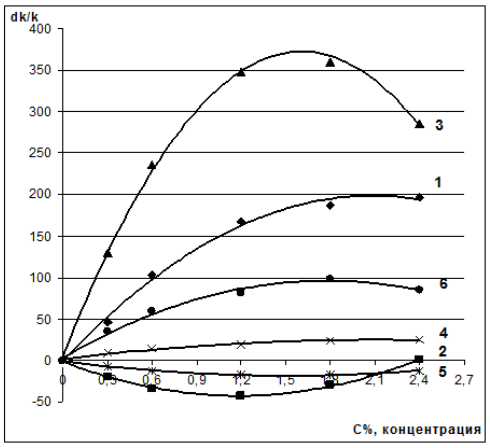
The choice of metal ions is determined by the fact that they are located in the fifth row of the D.I. Mendeleev periodic table, and are d-metals. Exception was made for a toxic and carcinogenic Cr^{+2}. From the perspective of biocidity, salt Cu (II) was taken, which is also a d-metal.

Dyeability results have been estimated by the method described above.

Changes of the structure of the polypeptides take place in the dyeing process, usually accompanied by partial destruction, which is related to some aggressive environments (pH, temperature). For this reason, the study of the effect of d-metal cations on the strength of silk by analyzing the structure of fibroin, dyed in the presence of d-metal ions, was of special interest.

Experimental data regarding changes in the color yield have shown that in some cases the use of metal cations is efficient, and saturation of colouring, on average, increases up to 8 times, as shown in Picture 4.

Investigation of influence of the number of electrons at the external energy level of d-metals in the dyeing processes for natural silk and wool with various dyes showed that the ability to increase the color yield possess the metals which have an intermediate number of electrons Mn^{+2} (5), Fe^{+2} (6 electrons), Co^{+2} (7 electrons).



1-VO^{+2}; 2- Mn^{+2}; 3- Fe^{+2}; 4-Co^{+2}; 5-Ni^{+2}; 6- Cu^{+2}

Picture 4

Analysis of the mass loss of samples from natural silk, dyed with direct and acid dyes, showed that strengthening of fibroin structure occurs by 3...4 times, while it should be noted that in all cases the introduction of metal ions of mass loss does not exceed the value corresponding to the mass loss of the uncolored sample.

Thus, we can conclude that the introduction of d-metal ions into the dye solutions used for silk painting and colouring of wool, in some cases not only improve the color yield, but also reinforce the fiber.

Assumption was made that metal ions fulfill a multifunctional role:

1. unsaturated external electron shell of d-metals enhances complexing properties, i.e. there is a possibility of formation of so-called complexes - "sandwiches" (dye - metal - fiber) . This interaction is accompanied by a change in color intensity, and studies have shown, in most cases, there is the deepening of dyeing;

2. ability of metals to interact with the fiber, with the formation of additional active sorption centers, involves participation of metals in "cross-linking" of neighboring molecules. Fibroin and keratin amino acids contain functional groups – OH, – COOH, - NH_2, with which metal ions, probably, form bonds of physical and chemical nature.

Likewise, attempt was made to analyze the effect of the number of electrons at the external energy level of d-metals being studied on the strength parameters of fibroin. There is a tendency to hardening of fibroin by using metal ions with the average number of electrons. It can be assumed that the nature of the dye, in addition to metals, has also a determining impact on the strength parameters of fiber.

The results of verification of resistance of obtained dyeings to operating conditions enable us to make a conclusion that the addition of d-metal cations are effective to improve fastness to washing, which increases by 1...2 points. Resistance to abrasion – 5 points. Furthermore, analysis of the lightfastness of dyed samples enables to make a conclusion that, in most cases, the presence of metal ions enhances fastness of obtained dyeing to light and weather by 1...2 points.

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