Mathematical planning of the experiment was used to develop a formulation for light stabilizers to improve the lightfastness of cotton knitted coloration, dyed with active dyes, in order to produce comfortable and high-quality knitted clothes. The variance and factor analyses of the experiment’s results were performed, which was carried out according to the scheme of the Latin cube of the first order involving the variation of factors – the type of light stabilizers and their concentration.

The technological mode of application of light stabilizers implied the impregnation of knitted fabric, drying, and thermal fixation of the material. For the dyed knitted samples, we have investigated the individual influence of light stabilizers on changing the color of the dyed knitted fabric and the kinetics of coloration photodegradation. The samples were isolated using the device with mercury-tungsten lamp RF 1201 BS (“REFOND”, China). Following the treatment and insolation, the general color differences of knittedwear samples were determined in comparison with the non-treated material, using the TCR-200 colorimeter (“PCE Instruments”, Germany).

The effectiveness of the developed formulation for light stabilizers was confirmed in the study of the lightfastness of knitted fabrics such as piqué weave, 1+1 eraser, smooth surface, dyed with active dyes of the brand Bezaktiv (“CHT Bezema”, Czech Republic). The result of our study is the developed formulation of light stabilizers consisting of 2,4-dihydroxy benzophenone, a UV-absorber, and hydroquinone, an antioxidant, at concentrations of 2 and 1 % of the material weight, respectively, which ensures an increase in the lightfastness of cotton knitted coloration by 52.9–66.8 % regardless of weave and active dye.

Keywords: cotton knitted, active dye, color differences, photodegradation kinetics, UV-absorber, antioxidant

1. Introduction

At present, the share of cotton and wool is significant in the structure of the world production of textile fibers; it is forecast to increase by 2030 despite the growing volume of artificial and synthetic fibers [1, 2]. This is due to that cotton is an indispensable raw material for the manufacture of summer and linen clothing assortment while wool clothing is associated with premium products; the increased consciousness consumption also plays a role.

Analysis of modern production indicators of textile products by types in the world shows that knittedwear manufacture volume exceeds that of woven fabrics [3–5]. This is due to the fact that knitted, owing to the knitted structure, is characterized by elasticity, thermal conductivity, by the capability to drape, and is indispensable in the manufacture of hosiery, underwear, sportswear. However, it should be noted that knitted clothes have significant shortcomings, the main of which is the loss of shape and strength of products, as well as the low resistance of dyes to the action of light and washing [6]. In addition, since in southern countries the period with a high level of the average daily amount of solar energy is long [7, 8], the effect of light on clothing during operation is maximally pronounced and causes destructive changes in both fiber-type materials and their coloration. Therefore, the production of knitted fabrics made of cotton for the summer and spring-autumn periods, which should have high indicators of lightfastness is necessary to meet the needs of consumers for high-quality and comfortable clothes.

Thus, it can be argued that the relevance of this study relates to the scientifically based solution to the task of developing technologies for improving the lightfastness of knitted fabrics made of natural fibers, which would provide consumers with high-quality and durable clothes.
It should be noted that most studies to render lightfastness properties to fiber-type materials address fabrics [9–13]. Thus, work [9] describes the detailed mechanisms of processes that occur during the photodegradation of most textile dyes. Taking into consideration modern achievements of organic chemistry, the synthesis of new classes of dyes and textile auxiliary substances, data on the mechanism of destruction under the influence of light, and the light protection techniques for dyed fiber-type materials should be supplemented and updated. A study reported in [10] gives a generalized mechanism of the photodegradation of active dyes on cotton; these results, however, need to be supplemented with ways to protect coloration from destruction under the influence of light.

Paper [11] reports the results of studying the influence of a commercially available light stabilizer, the cationic UV-absorber, on the coloration process of cotton fabric involving an active dye, as well as the lightfastness of the resulting colors. It was established that to increase the lightfastness of coloration, the specified light stabilizer should be used at a concentration of 4%; in this case, there is a change in the color shade.

The authors of article [12] investigated the lightfastness of cotton fabric coloration with active and direct dyes and the influence of individual absorbers of the ultraviolet (UV) radiation, as well as antioxidants, on the lightfastness of the coloration of fabrics made of cotton, dyed with active dyes [13]. 2-hydroxy benzophenone and phenyl salicylate were chosen as UV absorbers; organic acids, gallic, ascorbic, and caffeic, were selected as antioxidants. It was shown that the use of the studied light stabilizers in the concentration of 1 g/l after treatment at 70 °C for 30 minutes ensures a slight improvement in the lightfastness of cotton fabric coloration. In this case, the indicators of color differences amount to 1.36–6.35 units in only 36 hours of exposure to light.

Studies into the light stabilization of knitted materials, reported in papers [14, 15], are aimed at improving the protective properties of knitted materials against UV radiation relative to human skin. Based on the use of metal oxide nanoparticles, the authors of work [14] developed knitted fabrics with a high degree of protection against UV radiation and antibacterial properties. Study [14] reports a detailed study of the effect of the structural characteristics of knitted fabrics of different weaves on the factor of protection against UV radiation.

Thus, based on an analysis of the scientific literature, one can conclude that the issue of improving the lightfastness of knitted clothes coloration with the use of light stabilizers has remained unresolved. The development of light stabilization technology for the dyed cotton knitted fabric should be based on the mechanism of its destruction under the effect of light. The light stabilization of dyed fibrous materials is understood to be the protection of them against light and weathering, which cause the destruction of fibers, dyes, and finishing preparations, which are mostly polymers. Typically, polymers used in the final treatment of fibrous materials have a high atmosphere-, light- and heat resistance [16, 17]. With this in mind, one can conclude that the defining role in the process of photodegradation of dyed fibrous materials belongs to dyes and fibers.

It is known that the photo- and photo-oxidative destruction of cellulose proceeds with the formation of free radicals that are able to interact with the air’s oxygen and moisture with the formation of peroxides [18]. Under the influence of light, the polymeric molecules of cellulose undergo oxidation, accompanied by a decrease in the degree of their polymerization and, consequently, leads to the loss of mechanical strength by the fibrous materials [19, 20].

The degradation of textile dyes under the influence of light involves a two-stage mechanism of destruction [9, 10].

Stage I of dye photodegradation is photophysical, associated with the absorption of light by the dye’s molecule and its transition into a photo-excited state, which is more reactive than the molecule in the ground state. Photo-excitation is a reversible process; the excited molecule may not only enter the photochemical reactions leading to its destruction but also return to its original state. Thus, the first stage of photodegradation opens a path for light stabilization by preventing the formation of excited dye molecules. This is possible when using substances that can absorb [21–23] or shield [24–26] the most photoactive part of the spectrum.

Stage II of dye photodegradation is photochemical, associated with the chemical transformations of the excited molecule and causes its direct destruction or isomerization, which leads to loss of the original color or the coloration shade. Unwanted chemical transformations of the photo-excited dye molecule can occur not only during photochemical reactions but also in subsequent dark reactions after the termination of light effect. Those light stabilizers that are used to prevent stage II of dye photodegradation act by extinguishing photo-excited molecules [27, 28], or inhibiting photochemical reactions during the deactivation of active particles [29, 30].

An analysis of the two-stage mechanism of dye photodegradation taking into consideration the principles of action of known light stabilizers reveals that in order to ensure effective light protection of dyed knitted fabrics, simultaneous use of substances that operate at both stages of the photodegradation process is necessary.

Study [31] tested the effectiveness of using a series of individual UV absorbers and antioxidants for the light protection treatment of dyed cotton knitted fabrics. It was found that the examined substances, when used separately, provide for a slight increase in the lightfastness of colors as UV absorbers and antioxidants prevent the course of only one of the stages, which is ineffective. Thus, the authors experimentally proved the need for simultaneous use of UV absorbers and antioxidants in order to achieve effective light stabilization of the dyed cotton knitted fabric. In this case, it is advisable, when determining the optimal composition and the concentration of the components of the composition of light stabilizers in order to improve the lightfastness of cotton knitted fabrics, to employ the mathematical planning of the experiment.

3. The aim and objectives of the study

The aim of this study is to develop a formulation for light stabilizers to protect the coloration of cotton knitted fabrics against the action of light, which would make it possible to improve the wear resistance of knitwear during operation.

To accomplish the aim, the following tasks have been set: to define the main factors, the levels of their variation, and to mathematically plan an experiment based on the scheme of the first-order Latin cube;
– to conduct variance and factorial analyses of the experiment’s results and determine the effective formulation and the concentration of the components of the composition of light stabilizers;
– to investigate the effectiveness of using the developed formulation of light stabilizers to protect the coloration of cotton knitwear of different weave against the destructive action of light.

4. Materials and methods to develop a composition of light stabilizers to protect the coloration of cotton knitted fabrics against the effect of light

4.1. Characteristics of knitted fabrics, dyes, and light stabilizers
In this study, we used knitted fabrics made of 100% cotton of the following weaves: pique with a surface density of 170 g/m²; smooth surface with a density of 150 g/m², and eraser 1+1 with a surface density of 180 g/m².
The knitted wear was dyed with active dyes of the brand Bezaktiv Cosmos: Rot S-C, Blue S-C, and Gold S-C, which are bifunctional in terms of the chemical structure, with monochlorotriazine/vinyl sulfone active groups.
The characteristic of the UV absorbers and antioxidants is given in Table 1.

The cotton knitwear was treated with light stabilizers after being dyed with active dyes and rinsing the dyed knitted material. The technological mode of applying the studied light stabilizers implied the impregnation of knitwear with a solution of light stabilizers at a certain concentration, with the bath’s module \( M=20 \), for 15 minutes at a temperature of 25 °C. Next, the samples were pressed to the humidity of 100%, dried for 5 minutes at a temperature of 80 °C, and thermally fixed over 1 min. at a temperature of 150 °C.

The insolation of the knitted fabric samples treated with the light stabilizers was carried out at the device with mercury-tungsten lamp RF 1201 BS (“REFOND”, China).

4.2. Modes of treating a knitted cloth
A Bezaktiv Cosmos dye coloring mode is given in Table 2; a rinse mode after coloring – in Table 3.

After rinsing according to the above mode, the samples of knitted wear were dried.

4.3. Procedure of applying the mathematical planning of an experiment according to the scheme of a Latin cube
In order to determine the significance of the factors and the levels of factors, we performed the variance and factorial analyses of the results from the experiment, which was carried out based on the scheme of the first-order Latin cube [32, 33].

![Table 1](https://via.placeholder.com/150)

| Title | CAS number | Chemical formula | Physical appearance | Solubility in water/alcohol, g/l |
|-------|------------|------------------|---------------------|---------------------------------|
| UV-absorbers | | | | |
| 2,5-dihydroxy-acetophenone (DHAP) | 490-78-8 | ![DHAP chemical structure](https://via.placeholder.com/150) | yellowish powder | not soluble/well soluble |
| 2,4-dihydroxy-benzophenone (DHBP) | 131-56-6 | ![DHBP chemical structure](https://via.placeholder.com/150) | yellowish powder | 4.1/well soluble |
| phenylsalicylate (PS) | 118-55-8 | ![PS chemical structure](https://via.placeholder.com/150) | white crystals | not soluble/well soluble |
| Antioxidants | | | | |
| pyrocatechol | 120-80-9 | ![Pyrocatechol chemical structure](https://via.placeholder.com/150) | colorless crystals with weak odor | 461/well soluble |
| hydroquinone | 123-31-9 | ![Hydroquinone chemical structure](https://via.placeholder.com/150) | colorless crystals | 6.72/46.4 |
| resorcinol | 108-463 | ![Resorcinol chemical structure](https://via.placeholder.com/150) | white crystals with weak odor | well soluble/well soluble |

Preparation of solutions UV-absorbers was the use of a co-soluble - ethyl alcohol in a ratio with water 1:9.

![Table 2](https://via.placeholder.com/150)

| Coloring bath composition | Mode |
|--------------------------|------|
| Bath module \( M=50 \); | C    |
| A: Ultravon TC – 1 g/l; |      |
| sodium chloride – 20 g/l; |      |
| sodium carbonate – 10 g/l (20%); |      |
| B: dye – 0.5 % of the fabric’s mass; |      |
| C: sodium carbonate – 10 g/l (80%); |      |

The mode of cotton knitwear coloring technologies involving active dyes of the brand Bezaktiv Cosmos is given in Table 1.

![Table 3](https://via.placeholder.com/150)

| Rinse mode of cotton knitwear after coloring |
|--------------------------------------------|
| **Bath No.** | **Formulation** | **Mode** |
| 1 | Acetic acid 30% - 0.5 ml/l | \( T=50^\circ C, \tau=10\text{ min} \) |
| 2 | Hot water | \( T=70^\circ C, \tau=10\text{ min} \) |
| 3 | Eriopon R – 1 g/l | \( T=100^\circ C, \tau=10\text{ min} \) |
| 4 | Hot water | \( T=70^\circ C, \tau=10\text{ min} \) |
| 5 | Cold water | \( T=25^\circ C, \tau=10\text{ min} \) |

The insolation of the knitted fabric samples treated with the light stabilizers was carried out at the device with mercury-tungsten lamp RF 1201 BS (“REFOND”, China).
The variance analysis of the first-order Latin cube without repeated experiments employed the algorithm that determined the following:

1) the totals for all factors in each level according to formulae (1) to (12) and the values of the squares of these values:

\[ A_0 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ A_1 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ A_2 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ B_0 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ B_1 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ B_2 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ C_0 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ C_1 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ C_2 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ D_0 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ D_1 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

\[ D_2 = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9, \]

2) the sum of squares of all observations:

\[ SS_i = \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=1}^{2} y_{ijk}^2; \]

3) the sum of the squares of the totals for each factor divided by \( n^2 \):

\[ SS_f = \frac{1}{n^2} \sum_{i=1}^{2} X_i^2; \]

4) the correction term equal to the square of the grand total divided by the number of observations:

\[ SS_g = \frac{1}{n} \left( \sum_{i=1}^{2} A_i \right)^2 = \frac{1}{n} \left( \sum_{i=1}^{2} B_i \right)^2 = \frac{1}{n} \left( \sum_{i=1}^{2} C_i \right)^2 = \frac{1}{n} \left( \sum_{i=1}^{2} D_i \right)^2; \]

5) the sum of squares for all factors:

- the sum of squares due to factor \( A \):

\[ SS_A = SS_i - SS_g; \]

- the sum of squares due to factor \( B \):

\[ SS_B = SS_i - SS_g; \]

- the sum of squares due to factor \( C \):

\[ SS_C = SS_i - SS_g; \]

- the sum of squares due to factor \( D \):

\[ SS_D = SS_i - SS_g; \]

6) the total amount of squares equal to the difference between the sum of squares of all observations and the correcting term:

\[ SS_{tot} = SS_i - SS_g; \]

7) the residual sum of squares to assess experiment error:

\[ SS_{res} = SS_{tot} - (SS_A + SS_B + SS_C + SS_D); \]

8) the variances due to each factor separately and due to the interaction of factors:

\[ s_A^2 = \frac{SS_A}{(n-1)}, \]

\[ s_B^2 = \frac{SS_B}{(n-1)}, \]

\[ s_C^2 = \frac{SS_C}{(n-1)}, \]

\[ s_D^2 = \frac{SS_D}{(n-1)}, \]

\[ s_m^2 = \frac{SS_{res}}{(n^2-4n+3)}; \]

The significance of the factors’ influence was tested according to Fisher’s criterion based on the following inequalities:

\[ \frac{s_A^2}{S_m^2} \leq F_{p} (f_1, f_2), \]

\[ \frac{s_B^2}{S_m^2} \leq F_{p} (f_1, f_2), \]

\[ \frac{s_C^2}{S_m^2} \leq F_{p} (f_1, f_2), \]

\[ \frac{s_D^2}{S_m^2} \leq F_{p} (f_1, f_2), \]

where \( p \) is the level of significance; \( f_1, f_2 \) is the number of the degrees of freedom equal to \( f_1 = n-1, f_2 = (n-1)(n-2) \).

If the variance ratios satisfy inequalities (27) to (30), the corresponding factors are considered insignificant. If the variance ratio exceeds the tabular value, the influence of the factor is considered significant.

The factorial analysis of the results from our experiment was carried out by comparing the effects of the investigated factors at different levels using Duncan’s multiple rank criterion according to the following algorithm:

1) determine the average values of the generalized function of desirability \( Dn \) for each factor at all levels;

2) calculate the normalized error of the mean:

\[ s_b = \sqrt{\frac{s_m^2}{n}}; \]

3) rank the average values of the generalized function of desirability \( Dn \) by arranging in ascending order;
4) determine the values \((k-1)\) of the ranks for the selected level of significance \(p\) and the number of degrees of freedom \(f\), from Duncan’s table [32];

5) calculate the values \((k-1)\) of the smallest significant ranks by multiplying \((k-1)\) rank value by a normalized error of the mean;

6) check the significance of the difference between the averages of the generalized function of desirability \(D_{m}\), starting with the extreme in the ranking series (the largest and the least, the largest and the mean; the mean and the smallest) and compare the derived differences with the smallest significant ranks.

4.4. Procedure for converting experimental values of responses into a dimensionless scale of desirability

Constructing a desirability scale establishes a relationship between the feedback \(y_{u}\) values and its corresponding value of the partial desirability function \(d\). This problem includes one-way restrictions for the optimization criteria in the form \(y \leq y_{\text{max}}\) and \(y \geq y_{\text{min}}\). Exponential dependence (32) was used to convert the examined criteria \(y_{u}\) into partial desirability functions \(d\):

\[
d = \exp[-\exp(-y')] .
\]

where

\[
y' = b_0 + b_1y .
\]

The coefficients \(b_0\) and \(b_1\) can be determined by specifying for the two response values \(y\) the corresponding desirability \(d\) values mainly in the interval \(0.2 \leq d \leq 0.8\).

Having several responses converted to the scale \(d\), it is possible, by using computation, to combine some generalized desirability indicator \(D\) from these different \(d\). In this case, if at least one response is absolutely unsatisfactory, the generalized desirability function \(D\) should be equal to 0 regardless of the level of other responses.

4.5. Studying the effectiveness of using light stabilizers

We determined changes in the original color and lightfastness of the coloration of knitted fabrics by establishing the color differences \(\Delta E\) using the colorimeter TCR-200 ("PCE Instruments", Germany).

5. Results of developing the composition of light stabilizers to protect the coloration of cotton knitted fabrics against the action of light

5.1. Determining the formulation and the concentration of the components of the light stabilizers’ composition using the mathematical planning of the experiment

It is possible to determine the effective composition and the concentration of light stabilizers for the light protection of dyed cotton knitted fabric employing the mathematical treatment of experimental data when conducting the factorial and variance analyses [32]. In this case, we have chosen the following basic factors:

- the type of an antioxidant – pyrocatechol, hydroquinone, resorcinol;
- the concentration of an antioxidant – 0.5; 1; 2 %;
- the type of a UV-absorber – DHAP, DHB, PS;
- the concentration of a UV-absorber – 0.5; 1; 2 %.

Accordingly, Table 4 lists the factors and the levels of their variance that must be investigated.

| Factor designa | Factor designation | Factor variance level |
|----------------|--------------------|-----------------------|
| Factor         |                     | 0 | 1 | 2 |
| The type of an antioxidant | A | \(x_1\) | pyrocatechol | hydroquinone | resorcinol |
| The concentration of an antioxidant | B | \(x_2\) | 0.5 % | 1 % | 2 % |
| The concentration of a UV-absorber | C | \(x_3\) | 0.5 % | 1 % | 2 % |
| The type of a UV-absorber | D | \(x_4\) | DHAP | PS | DHB |

Thus, taking into consideration the number of factors and levels of their variation, for our factorial and variance analyses it is advisable to use the first-order Latin cube, at which all factors are set at the same number of levels. Factors \(A, B, C, D\) have three levels: 0, 1, 2.

The planning matrix for the first-order Latin cube is given in Table 5.

| Implementation plan of the first-order Latin cube |
|-----------------------------------------------|
| Formulation No. | Factor | Optimization criterion |
|  | \(x_1\) | \(x_2\) | \(x_3\) | \(x_4\) | \(h_1\) | \(y_2\) |
| 1 | pyrocatechol | 0.5 % | 0.5 % | DHAP | 4.32 | 1.05 |
| 2 | pyrocatechol | 1 % | 0.5 % | PS | 5.15 | 3.91 |
| 3 | pyrocatechol | 2 % | 0.5 % | DHB | 3.69 | 1.23 |
| 4 | hydroquinone | 0.5 % | 0.5 % | DHAP | 3.97 | 1.49 |
| 5 | hydroquinone | 1 % | 0.5 % | PS | 5.02 | 3.12 |
| 6 | hydroquinone | 2 % | 0.5 % | DHB | 2.15 | 2.69 |
| 7 | resorcinol | 0.5 % | 0.5 % | PS | 5.22 | 3.41 |
| 8 | resorcinol | 1 % | 0.5 % | DHB | 4.67 | 1.63 |
| 9 | resorcinol | 2 % | 0.5 % | PS | 4.5 | 2.09 |
| 10 | pyrocatechol | 0.5 % | 1 % | DHB | 1.94 | 2.51 |
| 11 | pyrocatechol | 1 % | 1 % | DHB | 3.52 | 2.97 |
| 12 | pyrocatechol | 2 % | 1 % | PS | 4.22 | 3.10 |
| 13 | hydroquinone | 0.5 % | 1 % | PS | 4.01 | 2.06 |
| 14 | hydroquinone | 1 % | 1 % | DHB | 1.82 | 1.94 |
| 15 | hydroquinone | 2 % | 1 % | DHB | 3.11 | 1.82 |
| 16 | resorcinol | 0.5 % | 1 % | DHB | 3.75 | 1.98 |
| 17 | resorcinol | 1 % | 1 % | PS | 4.66 | 4.80 |
| 18 | resorcinol | 2 % | 1 % | DHB | 3.16 | 1.86 |
| 19 | pyrocatechol | 0.5 % | 2 % | PS | 4.63 | 5.25 |
| 20 | pyrocatechol | 1 % | 2 % | DHB | 1.23 | 2.77 |
| 21 | pyrocatechol | 2 % | 2 % | DHB | 2.46 | 2.23 |
| 22 | hydroquinone | 0.5 % | 2 % | DHB | 2.35 | 2.21 |
| 23 | hydroquinone | 1 % | 2 % | DHB | 1.06 | 1.52 |
| 24 | hydroquinone | 2 % | 2 % | PS | 4.04 | 5.56 |
| 25 | resorcinol | 0.5 % | 2 % | DHB | 1.99 | 2.33 |
| 26 | resorcinol | 1 % | 2 % | DHB | 2.88 | 2.81 |
| 27 | resorcinol | 2 % | 2 % | PS | 5.16 | 8.25 |
| not treated with light stabilizers | | | | | 5.30 | 0 |
The criteria for optimizing the experiment included the lightfastness of the dyed cotton knitted fabric and a change in the initial coloration. These characteristics were established in determining the color differences of knitted samples after the insolation over 320 hours ($y_1$) and color differences of material samples after coloring ($y_2$). The results of the experiment are given in Table 5.

The study was carried out using a pique weave knitwear dyed by the active Bezaktiv Cosmos S-C dye at a concentration of 0.5% of the material's mass in the dye bath.

It was found [31] that individual substances exert a heterogeneous effect on the change in the original color of the dyed cotton knitted fabric and lightfastness. Given this, it was decided to further determine the optimal composition of light stabilizers on the basis of using a generalized Harrington's desirability function. For the indicator $y_1$, the response value obtained in the study of a raw knitwear sample is assigned the value of desirability 0.2, and the best value of the response obtained from the planning matrix (No. 23, Table 5) is assigned a desirability value of 0.8. For the indicator $y_2$, the value of the response obtained in the study of a raw sample of knitwear is assigned a value of desirability of 0.8, and the worst value of the response (No. 27, Table 5) is assigned a value of desirability of 0.8. The resulting values of optimization criteria and the partial desirability functions are given in Table 6.

By fitting the value $d$ in equation (31), we obtain:

$$0.8 = \exp[-\exp(-y')] + 0.2 = \exp[-\exp(-y')]$$

Hence, $y' = 1.500; y' = -0.476$. By fitting the calculated values $y'$, in equation (32), we obtain the systems of equations whose computation determines the coefficients $b_0$ and $b_1$ for each criterion. The computation results are given in Table 7.

The results of the experiments, given in Table 5, were recalculated according to the formulae in Table 4 into the partial functions of desirability $d_n$. The resulting numerical values of the partial functions of desirability for the criteria studied and the values of the generalized functions of desirability for each experiment, determined from formula (33), are given in Table 8.
The results of determining the average values of the generalized function of desirability $D_n$ for factors at all levels are given in Table 11.

The results of the variance analysis

| Variance source  | Number of degrees of freedom | Sum of squares | Mean square |
|------------------|------------------------------|---------------|------------|
| Factor A         | $(n-1)$                       | $SS_A = 0.035$| $\frac{SS_A}{\nu} = 0.017$ |
| Factor B         | $f = (n-1) = (3-1) = 2$       | $SS_A = 0.011$| $\frac{SS_A}{\nu} = 0.005$ |
| Factor C         | $f = (n-1) = (4-1) = 3$       | $SS_A = 0.227$| $\frac{SS_A}{\nu} = 0.113$ |
| Factor D         | $f = (n-1) = (5-1) = 4$       | $SS_A = 0.381$| $\frac{SS_A}{\nu} = 0.191$ |
| Rest             | $f = (n^2 - 4n + 3) = \frac{(27 - 12 + 3) = 18}{(7)}$ | $SS_m = 27.943 \times 10^{-4}$ | $\frac{SS_m}{\nu} = 1.553 \times 10^{-4}$ |
| Total            | $f = (n^2 - 1) = (27 - 1) = 26$ | $SS_m = 0.657$ | $\frac{SS_m}{\nu} = -$ |

The type of an antioxidant:

- $D_{\nu}^1 - D_{\nu}^0 = 0.308 - 0.254 = 0.054 \geq 0.013$ - the difference is significant;
- $D_{\nu}^1 - D_{\nu}^2 = 0.308 - 0.298 = 0.010 \leq 0.012$ - the difference is insignificant;
- $D_{\nu}^2 - D_{\nu}^0 = 0.298 - 0.254 = 0.044 \geq 0.013$ - the difference is significant.

Since the difference between the averages of the generalized desirability function $D_n$ at the factors’ levels 0 and 2 differs greatly from the value at level 1, while similar among themselves, we choose levels 0 and 2 for the factor. That is, we consider the antioxidants hydroquinone and pyrocatechol to be effective.

The type of a UV-absorber: (the concentration of a UV-absorber):

- $D_{\nu}^1 - D_{\nu}^0 = 0.323 - 0.279 = 0.044 \geq 0.013$ - the difference is significant;
- $D_{\nu}^1 - D_{\nu}^2 = 0.323 - 0.282 = 0.041 \geq 0.013$ - the difference is significant;
- $D_{\nu}^2 - D_{\nu}^0 = 0.282 - 0.279 = 0.003 \leq 0.012$ - the difference is insignificant.

The differences between the averages of the generalized desirability function $D_n$ for the factor $x_2$ at level 1 differ greatly from the values at levels 0 and 2 that are similar to each other. Thus, for the factor $x_2$ (the concentration of an antioxidant), we choose level 1–1%.

For the factor $x_2$ (the concentration of a UV-absorber):

- $D_{\nu}^1 - D_{\nu}^0 = 0.313 - 0.285 = 0.028 \geq 0.013$ - the difference is significant;
- $D_{\nu}^2 - D_{\nu}^0 = 0.313 - 0.306 = 0.007 \leq 0.012$ - the difference is insignificant;
- $D_{\nu}^1 - D_{\nu}^2 = 0.306 - 0.285 = 0.021 \geq 0.013$ - the difference is significant.

The resulting inequalities show that the difference between the averages of the generalized desirability function $D_n$ at the factors’ levels 1 and 2 differs greatly from the value at level 0; and, among themselves, they differ slightly. This makes it possible to choose, for factor $x_4$ (the concentration of a UV-absorber), levels 1 and 2 as optimal. That is, we consider the concentrations of UV absorbers of 1 and 2 (the type of a UV-absorber), levels 1 and 2 as optimal. That is, we consider the antioxidants hydroquinone and pyrocatechol to be effective.

For factor $x_4$ (the type of an antioxidant):

- $D_{\nu}^1 - D_{\nu}^0 = 0.460 - 0.184 = 0.276 \geq 0.013$ - the difference is significant;
- $D_{\nu}^1 - D_{\nu}^2 = 0.460 - 0.450 = 0.010 \leq 0.012$ - the difference is insignificant.
The difference between the averages of the generalized desirability function $D_n$ for the factor $x_4$ at levels 0 and 2 differs greatly from the value at level 1; among themselves, they are similar. Given this, we choose levels 0 and 2 for this factor. That is, UV absorbers DHAP and DHPB are effective.

Thus, based on the variance and factorial analyses of the experiment (Table 5), the following compositional formulations for the light stabilizers were selected, in which the significant levels of the factors studied coincide:

- No. 11) pyrocatechol 1 %+DHAP 1 %
- No. 14) hydroquinone 1 %+DHPB 1 %
- No. 20) pyrocatechol 0.5 %+DHPB 1 %
- No. 23) hydroquinone 1 %+DHPB 2 %

Fig. 1 shows the results of studying the influence of the developed formulations of light stabilizers on the photodegradation kinetics of dyed knitwear.

An analysis of the resulting kinetic curves of photodegradation (Fig. 1) reveals that the selected compositions of light stabilizers significantly slow down the process of destruction of the active dye on the cotton knitwear. In this case, the lowest indicators of color differences are observed for the sample of knitwear treated with formulation No. 23.

Thus, by performing the variance and factorial analyses of our experiment and investigating the kinetics of photodegradation of the coloration of cotton knitwear, we selected the formulation of the light stabilizers that least affects the coloration and ensures its highest lightfastness. The formulation of light stabilizers consists of a UV-absorber, DHBF, and an antioxidant, hydroquinone, at a concentration of 2 and 1 % of the material weight, respectively.

5.2. Studying the influence of the developed formulation of light stabilizers on the lightfastness of cotton knitted fabric

Fig. 2. shows the kinetic curves of photodegradation for the knitted samples of pique weave, dyed by various active dyes, for those non-treated, and those dyed by the developed formulation of light stabilizers.

A comparison of the resulting photodegradation kinetic curves of the dyed knitwear shows that the treatment with the developed composition of light stabilizers contributes to a significant reduction of photodegradation of coloration regardless of the active dye.

The indicators of color differences in the coloration of cotton knitwear weave pique, eraser 1+1, and smooth surface samples, which are achieved after 320 hours of insolation, dependent on the color of the active dye and the treatment with the composition of light stabilizers are given in Table 13.

The results obtained allow us to conclude that the treatment with the developed formulation of light stabilizers slows down the process of destruction of dyes under the influence of light on knitwear of different weaves. Thus, after 320 hours of insolation, color differences for the knitted fabrics’ explored weaves, dyed by Bezaktiv Cosmos Rot S-C, are 8.16–9.81 units, and, after being treated with the composition of light stabilizers, decrease to 3.24–3.79 units. The decrease in the color differences of knitwear after being treated with the composition for protection against light and insolation is also observed for the coloration obtained when using Bezaktiv Cosmos Blue S-C and Bezaktiv Cosmos Gold S-C, regardless of the weave of the cloths.
Fig. 3 shows the results of calculating the relative decrease in the indicators of the color differences of knitwear, treated with the composition of light stabilizers, compared to non-treated samples after 320 hours of insolation.

It was established that the treatment of knitted fabrics of different weaves with the developed composition of light stabilizers helps reduce the relative indicators of color differences in knitwear by 52.9–66.8% depending on the dye and weave of the material.

Table 13

| Dye                     | Treatment option                        | Color differences, dE |
|-------------------------|-----------------------------------------|-----------------------|
|                         | pique | eraser +1 | smooth surface     |
| Bezaktiv Cosmos Rot S-C | treated with the composition of light stabilizers | 3.56 | 3.79 | 3.24 |
|                         | non-treated | 9.81 | 9.20 | 8.16 |
| Bezaktiv Cosmos Blue S-C | treated with the composition of light stabilizers | 2.98 | 3.15 | 2.64 |
|                         | non-treated | 8.97 | 6.69 | 6.17 |
| Bezaktiv Cosmos Gold S-C | treated with the composition of light stabilizers | 2.20 | 2.27 | 1.82 |
|                         | non-treated | 5.50 | 5.09 | 4.90 |
6. Discussion of results of developing the formulation of light stabilizers to protect dyed cotton knitwear against light

The development of the formulation of light stabilizers in order to render lightfastness to the dyed cotton knitwear involved the mathematical planning of the experiment using the first-order Latin cube. This scheme of the experiment was chosen because the factors vary at the same number of levels. The factors of the experiment selected were the type of an antioxidant and a UV-absorber and their concentrations. The results from the variance analysis of our experimental data showed that the studied factors are significant when investigating their effect on the lightfastness and change of the initial coloration of cotton knitwear.

The factorial analysis of the experiment’s results has allowed us to choose effective formulations for those light-stabilizing compositions that ensure the slightest change in the original color and the highest lightfastness of the coloration of cotton knitwear. It was found that the effective UV absorbers are, in this case, DHAP and DHBP, the antioxidants — pyrocatechol and hydroquinone. PS and resorcinol demonstrated worse results. Different effectiveness of the studied light stabilizers can be explained on the basis of the mechanisms of their light protection action relative to the coloration of knitwear.

DHAP refers to ketones, which, when exposed to UV radiation, dissociate at breaking the \( C=O \) bond [34]. The photochemical properties of DHAP derivatives can be characterized by the UV-visible and fluorescent spectra, as well as quantum fluorescence output. Two bands that correspond to two \( \pi-\pi^* \) orbitals were found in the UV-visible spectra of DHAP derivatives based on the computation using kinetic theory of functional density. At the same time, these substances demonstrate a very weak fluorescence, as evidenced by the low values of measured quantum outputs [35]. The decrease in the quantum fluorescence output is due to the phenomenon of effective intramolecular proton transfer in an excited state [36].

Most commonly, the acid group in these reactions is phenolic OH-group, whereas the main location is usually heteroatom, such as carbonyl oxygen or nitrogen heterocycle. Thus, under the influence of UV radiation, as a result of the intramolecular transfer of protons in the excited state, DHAP can move from enol to keto-form according to the scheme given in Fig. 4.

The photochemistry of DHBP derivatives has been studied in more detail than other classes of UV absorbers. It is known that the keto-structure quickly turns into the structure of the photo-enol by absorbing light (Fig. 5). The return of the photo-enol structure to the structure of ketone occurs with the loss of energy in the form of heat, which ensures the high efficiency of the process. The rapid and effective phototautomerism of DHBP is explained by the existence of an intramolecular hydrogen bond in both structures [37].

PS is characterized by very low absorption in the UV spectrum region. However, after the short exposure to sunlight, there is an increase in its absorption in the range of 290–400 nm, and, after prolonged light, its spectrum resembles the spectrum of DHBP derivatives [38]. Thus, PS demonstrates its effectiveness during the protection of coloration against light by regrouping, which is caused by the action of light, and during which it is converted into a derivative of DHBP according to the scheme shown in Fig. 6.

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Fig. 3. The effect of the developed composition of light stabilizers on the relative decrease in the indicators of color differences in the coloration of knitwear of different weave after 320 hours of insolation

Fig. 4. The mechanism of DHAP transformation under the influence of light

Fig. 5. The mechanism of DHBP transformation under the influence of light

Fig. 6. The mechanism of PS transformation into a DHBP derivative under the influence of light
Next, under the influence of UV radiation, there is a keto-enol regrouping of the DHBP derivative, formed from PS, which ensures the effectiveness of the light-absorbing action of PS (Fig. 7).

Two-atom phenols – hydroquinone, resorcinol, pyrocatechol – are common in nature and are part of many natural compounds. Multiatomic phenols are weak OH-acids and easily enter the reactions of electrophilic substitution and oxidizing [34, 39]. The oxidizing of diphenols with para- and ortho-arrangement of hydroxyl groups – hydroquinone and pyrocatechol – leads to the formation of para- and ortho-quinones, respectively (Fig. 8).

The processes of hydroquinone and pyro-catechin oxidation are reversible and yield well-reproduced electrode potentials whose magnitude depends on pH [40].

Resorcinol is more resistant to oxidation. It should be noted that resorcinol cannot form meta-quinones, and its oxidation leads to the formation of a complex mixture of products [39, 40]. The presence in the aromatic core of resorcinol of the two hydroxyl groups in the meta-position leads to the mutual strengthening of their activating action, which causes the extreme activity of resorcinol in the reactions of electrophilic substitution. For this reason, resorcinol is highly reactive to electrophilic agents [39, 40]. Resorcinol at certain concentrations can demonstrate antioxidant activity associated with the formation of hydroxyquinone according to the scheme shown in Fig. 9 [41, 42].

The antioxidant properties of diphenols are associated with the presence of movable hydrogen atoms in hydroxyl groups in their structure, which easily release it when interacting with free radicals. In this case, phenols act as the reducers of free radicals, turning into less-active phenoxy radicals [42, 43].

Thus, the low efficiency of PS as a UV-absorber can be explained by the fact that the substance undergoes a two-stage transformation under the influence of UV radiation. First, a derivative of DHBP is formed, which is capable of keto-enol regrouping during light absorption. The less effective effect of resorcinol as an antioxidant is caused by its increased resistance against oxidation compared to hydroquinone and pyro-catechin.

The results from our factorial analysis of experimental data have shown that effective light stabilizer formulations include DHAP or DHBP as a UV absorber and hydroquinone or pyro-catechin as an antioxidant. The optimal concentrations of UV absorbers are 1 or 2 %, antioxidants – 1 % of the material’s weight. Thus, we have chosen those formulations of light stabilizers for which the factors’ significance levels coincided.

As regards the defined compositions of UV absorbers and antioxidants, we investigated changes in the original color and the photodegradation kinetics of the coloration of cotton knitwear of the pique weave, dyed by the active dye Bezaktiv Cosmos Gold S-C. An analysis of the kinetic curves of photodegradation (Fig. 1) reveals that the lowest indicators of color differences after the insolation of knitwear samples are demonstrated by the formulation containing DHBP and hydroquinone in the amount of 2 and 1 %, respectively.

Consequently, based on the variance and factorial analyses of the experiment conducted according to the scheme of a Latin cube, as well as additional research into the kinetics of photodegradation of the coloration of cotton knitwear, the formulation of the effective composition for light stabilizers was selected. It consists of the UV-absorber DHBP and the antioxidant hydroquinone at a concentration of 2 and 1 % of the material’s weight, respectively.

In order to confirm the effectiveness of the developed composition of light stabilizers, the kinetics of the coloration photodegradation of knitwear with a pique weave (Fig. 2) were investigated. In addition, we established the indicators of color differences in the coloration of knitwear of different weaves after 320 hours of insolation (Table 13, Fig. 3).

Our results show that the developed formulation for light stabilizers, which contains DHBP and hydroquinone in the amount of 2 and 1 %, respectively, helps improve the lights fastness of cotton knitwear coloration regardless of weave and active dye. At the same time, the indicators of color differences of knitwear after being treated with the developed composition are reduced by 52.9–66.8 % depending on the dye and weave of knitwear.

The resulting indicators of color differences in the coloration after being treated with the light-stabilizing formulation characterize the lightfastness of knitwear of the explored weaves and coloration, when using dyes of the brand Bezaktiv Cosmos, which is the main limitation of this study.

In the future, it is promising to study the influence of the developed formulation of the UV-absorber and antioxidant on the lightfastness of coloration when using other classes of dyes on cotton fabric and knitwear.
In addition, it is necessary to investigate the resistance of the resulting light protective effect under the conditions of using summer knitwear under the influence of washing and sweat.

7. Conclusions

1. The main factors that we chose, on which the effectiveness of the formulation of light stabilizers depends, are the type and concentration of a UV-absorber and an antioxidant. The UV absorbers selected were 2,5-dihydroxyacetophenone, 2,4-dihydroxy benzophenone, and phenyl salicylate; the antioxidants – pyro-catechin, hydroquinone, and resorcinol, at concentrations of 0.5; 1; 2 %. Taking into consideration the factors and the levels of their variance, we mathematically planned the experiment according to the scheme of the first-order Latin cube.

2. The variance and factorial analyses of the experiment’s results were carried out; it has been determined that the formulation of light stabilizers, which slightly affects the initial change in the coloration of the cotton knitted fabric and improves its lightfastness is effective. The developed composition consists of the UV-absorber 2,4- dihydroxy benzophenone and the antioxidant hydroquinone, at concentrations of 2 and 1 % of the material's weight, respectively.

3. The analysis of results of our study into the kinetics of photodegradation of the coloration of knitted weave samples of pique weave, dyed by various active dyes, as well as the indicators of color differences in the coloration of knitted fabrics of different weaves, dyed by various active dyes of Bezaktiv brand, after 320 hours of insolation, indicate the effectiveness of the developed formulation for light stabilizers.

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