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Photochromic and Thermochromic Systems with Negative Chromism

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Abstract—The analysis of study results in the field of the development of reversibly bleaching photochromic and thermochromic compounds and systems based on them for creating coatings of the chameleon type is presented.

Keywords: photochromism, thermochromism, negative chromism, absorption spectra, color, transformation mechanism

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INTRODUCTION

There has been heightened interest recently in coatings for various purposes that dynamically and reversibly change their color, due to the improvement of coatings that adapt to the color of the surrounding landscape, as well as the creation of multifunctional clothing and theatrical scenery that change color depending on the illumination and the tasks set.

These problems can be solved using so-called smart materials, which include photo-, thermo-, and electrochromic systems that reversibly change their color, like chameleons, under the action of light, heating and passing an electric current, respectively. If such coatings are used, they, like the skin of living reptiles, can mimic, adapting to changes in the color of the surrounding landscape. Until recently, it was difficult to solve this problem due to the lack of chromic materials-chameleons with acceptable properties.

Work on the use of these photo-, thermo-, and electrochromic substances and materials based on them began to develop intensively in the 70s of the last century. The existing range of chromic substances and the ability to control the spectral properties of materials using computer technology make it possible to purposefully change their color with high accuracy.

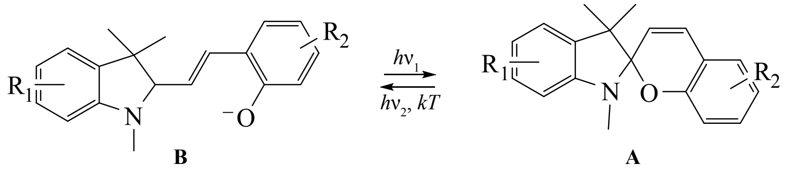
At this time, both in Russia and abroad, a large range of photochromic, thermochromic and electrochromic substances and systems based on them has been created for various purposes including organic and inorganic substances, on a flexible basis in particular, providing reversible control of optical properties using external influences.

The analysis of the results of the development of photochromic and thermochromic substances and systems with negative chromism (reversibly discoloring under the exposure to light and heat, respectively) is presented below. In contrast to photochromic systems with positive photochromism (which are reversibly colored under the action of UV light and when heated) they are the most promising for creating chameleon fabrics.

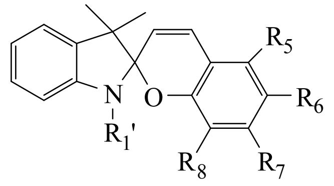
Chromic Substances and Systems for Camouflage Coatings

Photochromic substances and systems. There is a significant variety of photochromic organic substances that differ in the mechanisms of photochromic transformations and photoinduced color changes that depend on the structure of compounds [1]. The distinctive features of organic photochromic systems are the selectivity of their absorption, which ensures the production of tissues with different shades of color, as well as high

Scheme 1.



Scheme 2.



coefficients of molecular extinction of the initial and photoinduced forms, which makes it possible to obtain highly photosensitive materials of micron thickness. The main disadvantages of photochromic organic materials that limit their application areas include the low resistance of most organic compounds to irreversible photochemical and thermal transformations. However, the effect of intense activating irradiation on the colored state of substances with negative photochromism is minimal, since they pass into a weakly colored and even colorless state. Consequently, the limited exposure to irradiation that is harmful to colored organic substances becomes less effective compared to photo-coloring photochromic substances with positive photochromism. This leads to an increase in the service life of photochromic materials with negative photochromism in sunlight.

Photochromic substances exhibiting negative photochromism are less studied than compounds with positive photochromism [2, 3].

Among the existing substances, a number of compounds from the class of spiropyrans exhibit negative photochromism (Scheme 1).

In contrast to the positive photochromism of spiro compounds (spiropyrans and spirooxazines), the initial colored merocyanine form **B** under the action of visible light absorbed by this form turns into a photoinduced thermodynamically unstable colorless spiropyrane form **A**. This form spontaneously or under the effect of UV light turns into the original merocyanin form **B**. The process of spontaneous coloring is accelerated when the system is heated.

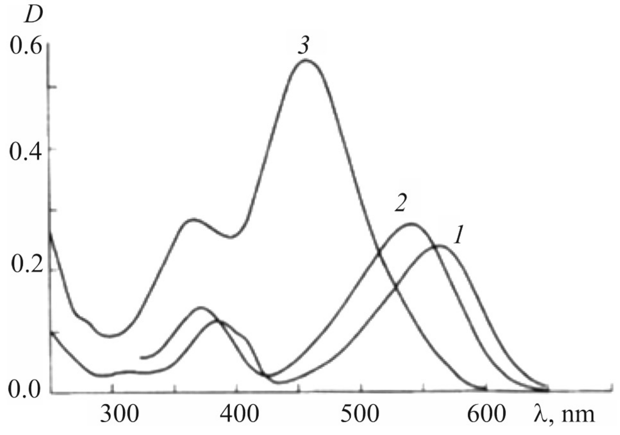


Fig. 1. Absorption spectra of spiropyran SP 1 ($R' = CH_3$; $R_5 = R_6 = R_7 = H$; $R_8 = COOH$) ($c = 2\times10^{-4}$ M) in chloroform (*1*), acetone (*2*), and ethanol (*3*) [4].

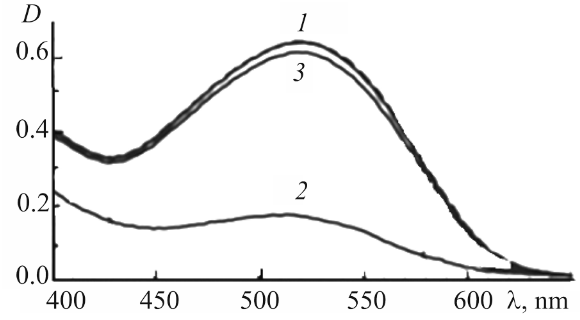


Fig. 2. The change of absorption spectra and color of an aqueous suspension of SiO_2 particles with spiropyran SP 2 ($R'_1 = N(CH_3)_3Br^-$; $R_5 = R_7 = R_8 = H$; $R_6 = NO_2$) before (*1*) and after irradiation with visible light (*2*) and subsequent exposure in the dark within 90 min.

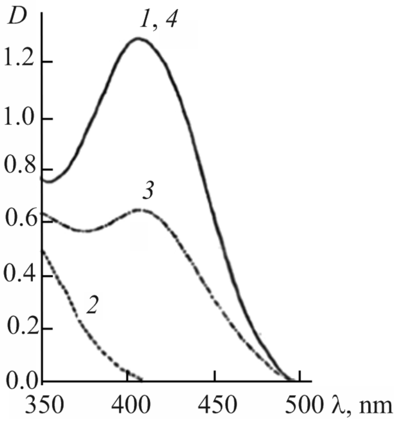


Fig. 3. Changes in the absorption spectra of the spiropyran SP 3 solution ($R' = CH_3$; $R_5 = R_8 = R_7 = H$; $R_6 = NO_2$) in acetone with the addition of malonic acid ($c = 1.1\times 10^{-4}$ M) before (*1*), after irradiation with visible light (*2*) and subsequent storage in the dark (*3*, *4*).

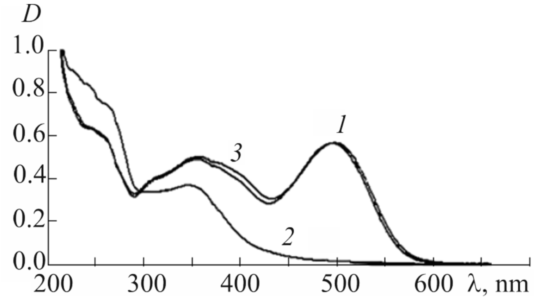


Fig. 4. Absorption spectra of spiropyran SP 4 in water before (*1*), after irradiation with visible light within 15 s (*2*) and subsequent thermal relaxation at 40°C (*3*).

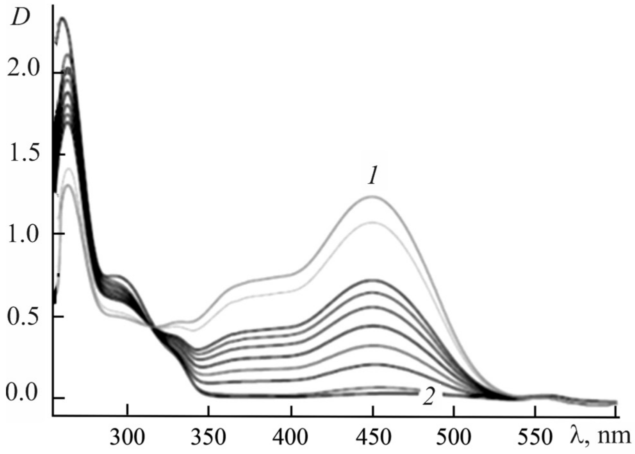


Fig. 5. Absorption spectra of spiropyran SP 8 in dimethyl sulfoxide before (*1*) and after (*2*) irradiation with visible light.

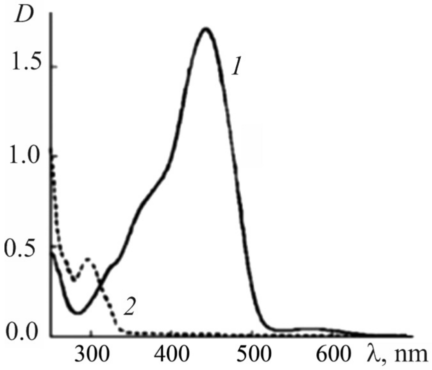


Fig. 6. Absorption spectra of spiropyran SP 10 in ethanol before (*1*) and after (*2*) irradiation with visible light.

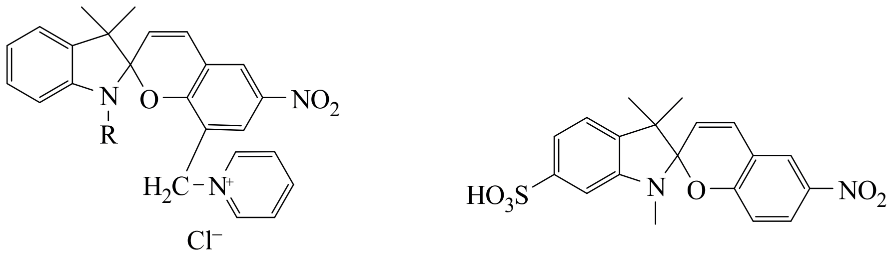
The greatest attention was paid to the study of the negative photochromism of indoline nitrosubstituted spiropyrans (Scheme 2).

The negative photochromism of these photochromic compounds is due to several reasons related to the shift of the equilibrium between the cyclic and merocyanine forms towards the latter [4]. The main reasons include the nature of substituents and the polarity of solvents (Fig. 1) [5], adsorption on the silica gel surface (Fig. 2) [6], hydrogen bonding [7], introduction into the polymer matrix [8], conjugation with macromolecules [9], the formation of complexes of merocyanine molecules with metal ions [10], as well as protonation of the merocyanine form of spiropyrans (Fig. 3) [11].

Photochromic spiropyrans with long-chain substituents at the nitrogen of the indoline fragment SP 4–SP 6 (Scheme 3) exhibit negative photochromism in aqueous solutions [12]. The most effective photochromic transformations were found for spiropyran with the shortest chain length SP 4 (Fig. 4). The disadvantage of these compounds is the low relaxation rate of the photoinduced cyclic form to the initial merocyanine state. An acceptable rate of thermal relaxation is observed only at a temperature not lower than 40°C.

Negative photochromism is manifested by sulfo-substituted spiropyrans SP 7–SP 9 (Scheme 3, Fig. 5) [13], as well as SP 10 (Fig. 6) [14].

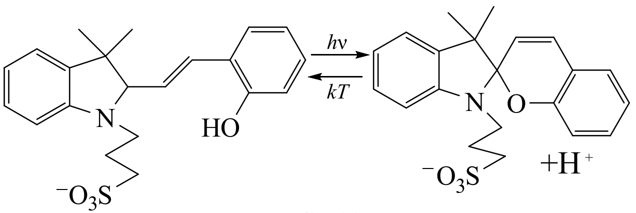
Scheme 3.



SP 4: R = C_8H_{17}; SP 5: R = $C_{12}H_{25}$;
SP 6: R = $C_{18}H_{37}$

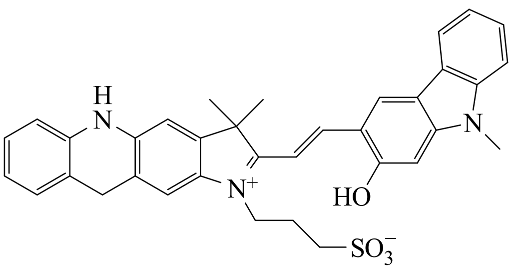
SP 7: R = H; SP 8: R = CH_3; SP 9: R = NO_2

Scheme 4.



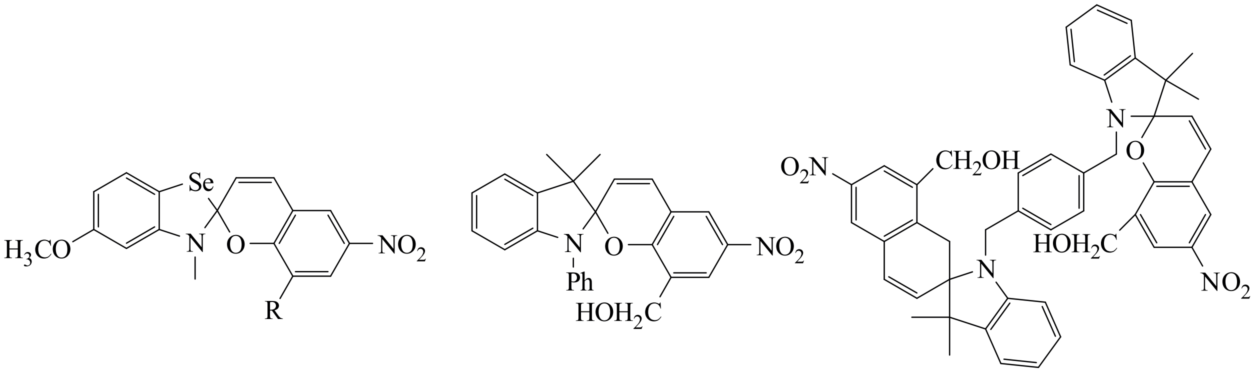
SP 10

Scheme 5.



SP 11

Scheme 6.



SP 12 SP 13 SP 14

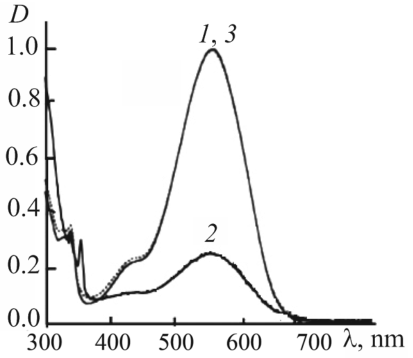


Fig. 7. Absorption spectra and coloring of the solution of spiropyran SP 11 in methanol before (*1*), after irradiation with visible light (*2*) and after the dark relaxation for 7 min (*3*).

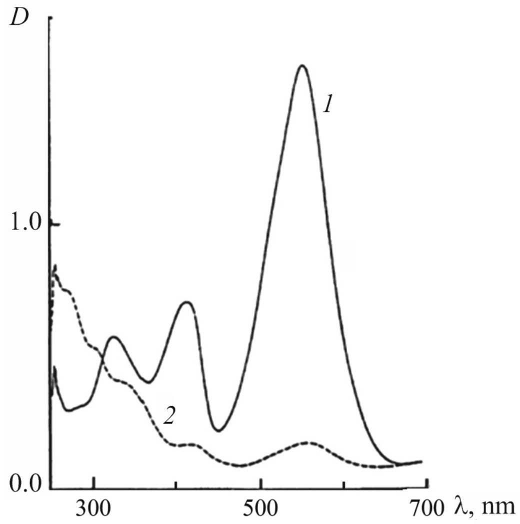


Fig. 8. Absorption spectra of spiropyran SP 12 in dimethylsulfoxide before (*1*) and (*2*) after irradiation with visible light.

In the case of spiropyran SP 10 (Scheme 4), when the solution is discolored by visible light, not only a cyclic form of the compound is formed, but a proton is also released. The absorption band of the original open form is located in the short-wave region of the spectrum.

To shift the absorption band of the original merocyanine form to a longer wavelength spectral region, spiropyran SP 11 (Scheme 5) was synthesized (Fig. 7) [15].

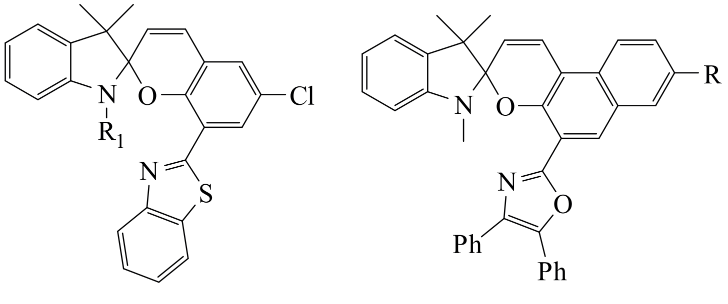
Similar photoinduced spectral changes were detected for the compound SP 12 (Scheme 6) (R = $CH_2OCOC(CH_3)=CH_2$), the absorption band of the initial merocyanine form of which is located at 554 nm (Fig. 8) [16]. Under the action of visible light, it disappears and at the same time there is a rearrangement of the absorption spectra in the UV spectral region.

The study results of complexes of molecules of hydroxymethyl-substituted spiropyrans SP 13 and SP 14 (Scheme 6) with ions of alkaline- and rare earth elements showed that the observed equilibrium shift towards the merocyanine form of the complexes and the hypsochromic shift of the absorption bands also depend on the structure of the compounds and the nature of the metal [17]. The spectral changes for the SP 13 compound are shown in Fig. 9 [18].

Negative photochromism is shown by complexes of metal cations with molecules of 8-benzothiazole-substituted spiropyrans SP 15 [19], as well as 5′-(4,5-diphenyl-1,3-oxazole-2-yl) substituted spiro[indolino]naphthopyranes) SP 16 and SP 17 (Scheme 7) [20].

Negative photochromism also occurs when spiropyrane molecules are introduced into polymer chains as side fragments. It is characteristic of a photochromic polymer with spiropyranic fragments of SP 18 (Scheme 8) in polar

Scheme 7.



SP 15 SP 16: R = H; SP 17: R = OCH_3

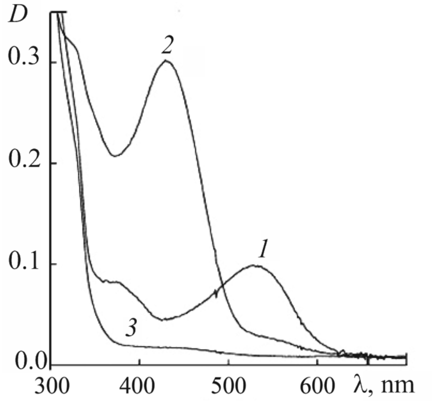


Fig. 9. Absorption spectra of the photochromic polymer SP 13 in water at 5°C before (*1*, *2*) and after irradiation with visible light (*3*) without (*1*) and in the presence of $Pb(ClO_4)_2$ (*3*).

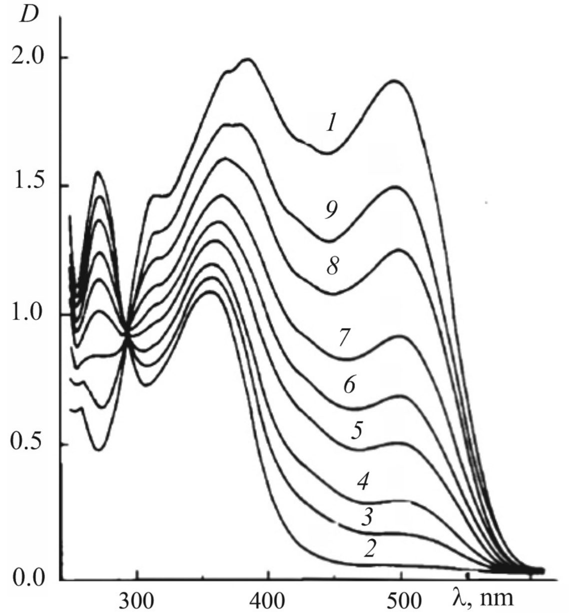


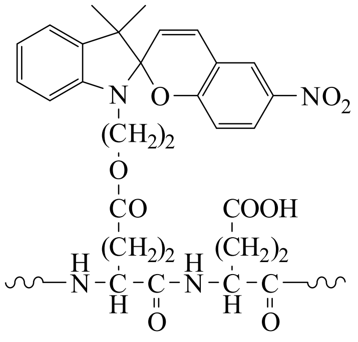
Fig. 10. Absorption spectrum of photochromic polymer SP 18 in hexafluoro-2-propanol before (*1*), after irradiation with visible light (*2*) and during the dark relaxation process (*3–9*).

hexafluoro-2-propanol in the presence of trifluoroacetic acid [5, 21, 22]. Before irradiation with visible light, three absorption bands are observed in the absorption spectrum of this polymer with maxima at 312, around 365–385 and at 495 nm (Fig. 10). When irradiated with visible light, the last two bands disappear, and the intensity of the short-wave absorption band increases.

Samples of tissue-based photochromic materials with reverse photochromism were produced using spiropyran SP 19 (Scheme 9) [23]. For this purpose, a cotton fabric was chosen. The samples were prepared by impregnating cotton fabric with a pre-prepared photochromic solution by various methods (immersion in the solution, watering, smearing). After impregnation, the sample was dried at room temperature in a chemical fume hood in the dark. The test of the obtained samples of photochromic materials was carried out using bright solar radiation or the light of a 60-watt incandescent lamp. To reduce the transition time to the initial state, the samples were heated in a drying cabinet at a temperature of 60°C for 2 min. The cyclicity of photochromic transformations was checked by alternating irradiation with visible light and thermal heating in a chemical fume hood. The photo-induced change in the spectral characteristics of one of the samples is shown in Fig. 11.

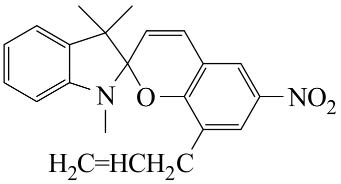
In recent years, cyano-substituted chromophores have appeared, resembling the merocyanin form of spiropyrans, which under the action of visible light

Scheme 8.



SP 18

Scheme 9.



SP 19

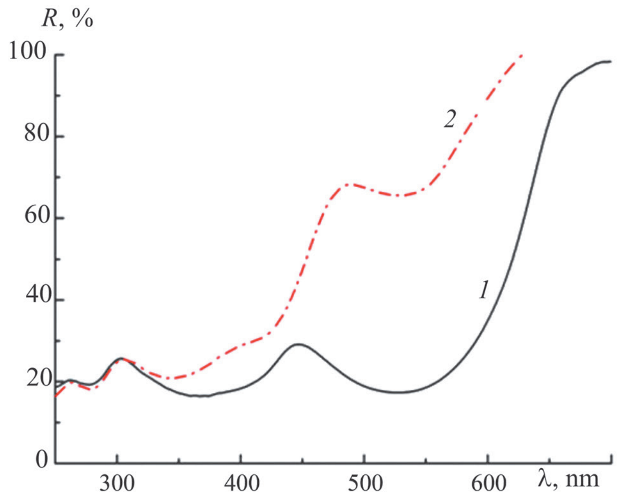


Fig. 11. Reflection spectra of a photochromic textile material sample before (*1*) and after irradiation with visible light (*2*).

experience a reversible transformation into a cyclic form (Scheme 10) [24–27].

A spectral-kinetic study of the negative photochromism of compounds of this type showed that, depending on the structure of the compounds, the initial merocyanine form may have different colors due to differences in spectral characteristics (Table 1).

Figure 12 shows the photoinduced change in the spectral characteristics of compound **1c** in ethanol.

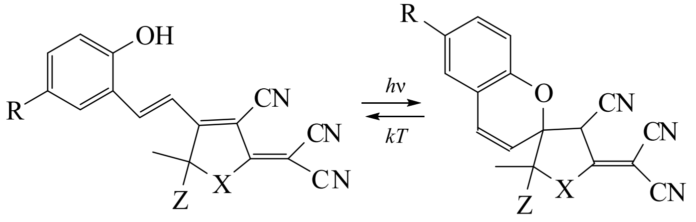
A variety of colors are distinguished by Stenhouse compounds (SC) that undergo reversible *cis-trans* isomerization, which is a spatial change in the position of the fragments of the molecule due to the non-free rotation of the parts of the molecule around the double bond (Scheme 11) [28, 29].

The photoinduced spectral changes of this compound in water are shown in Fig. 13.

Polymers with photochromic fragments from compounds of this type SC 1–SC 4 (Scheme 12) provide photochromic coatings with different initial colors that reversibly disappear under the influence of visible light [28, 30].

Among the group of photochromic compounds undergoing cis-trans isomerization, thioindigoid dyes have special properties [31], which, unlike the

Scheme 10.



X = O, H; R = H, NO_2, OCH_3; Z = Me, OH.

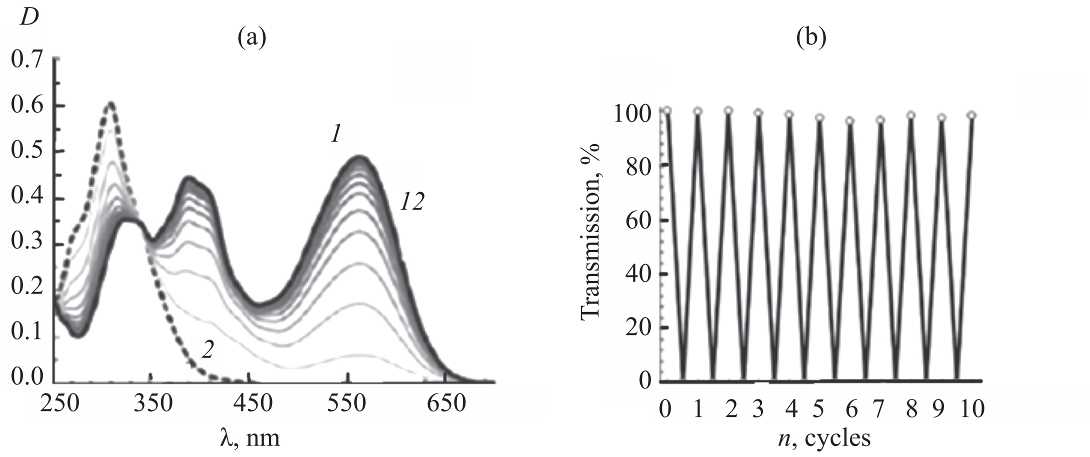
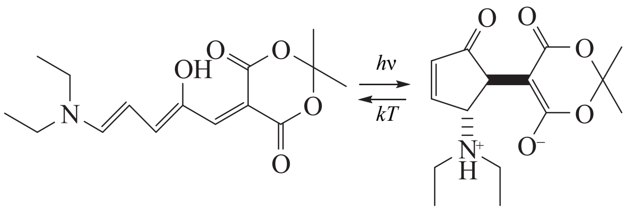


Fig. 12. Photoinduced spectral changes (a), the cyclicity of photochromic transformations (b) of compound **1c** solution in ethanol.

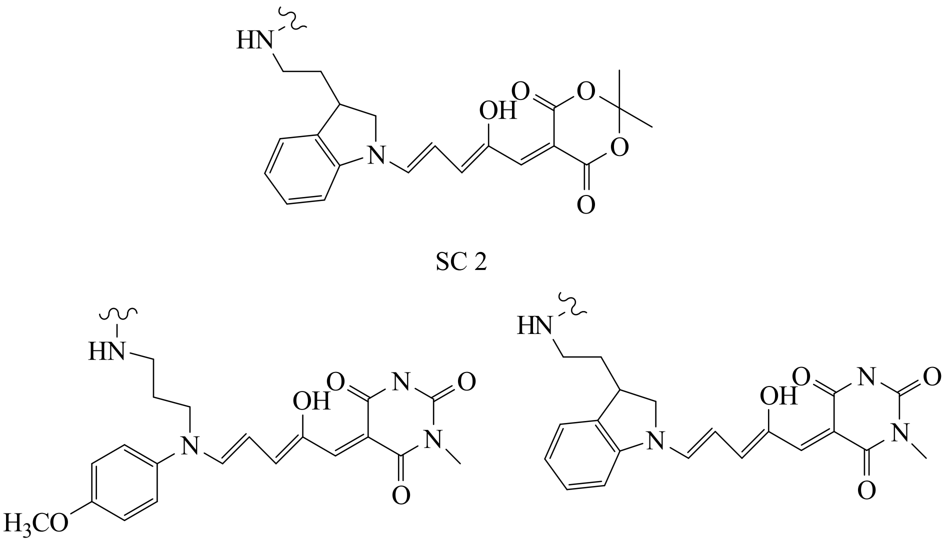
Scheme 11.



SC 1

A **B**

Scheme 12.



SC 2

SC 3 SC 4

photochromic compounds discussed above, do not photobleach, but change color under the influence of light (Scheme 13, Fig. 14).

The absorption spectra of both forms of these compounds are located in the visible region of the spectrum and are sharply separated (Fig. 14).

The photoinduced proton transfer is implemented in negative photochromic transformations of formazans (Scheme 14) [32].

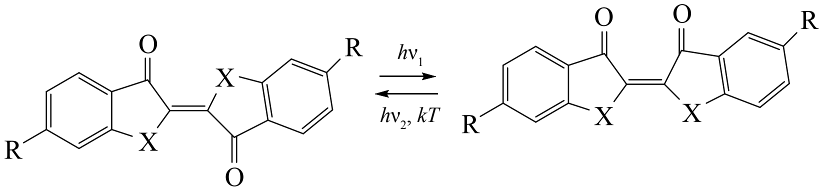
The reversible photoinduced spectral changes of one of these compounds are shown in Fig. 15.

Table 1. Spectral-kinetic properties of cyan-substituted chromophores in ethanol[a]

Compound no.	R	Z	X	$\lambda_{\max}$,nm	$\tau_{1/2}$, s
1a	H	Me	O	450	5
1b	H	OH	NH	426	3.5
1c	NO_2	Me	O	564	295
1d	NO_2	OH	NH	520	360
1e	MeO	Me	O	485	–
1f	MeO	OH	NH	456	–

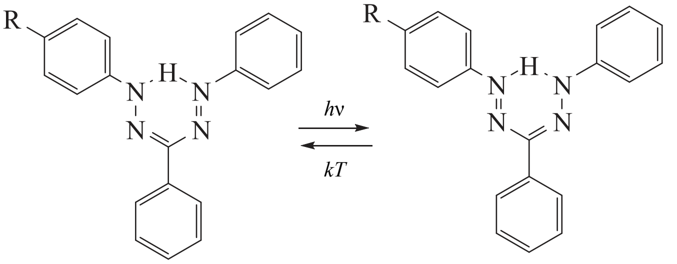
[a] $\lambda_{\max}$ is the wavelength of the maximum of the absorption bands of compounds before irradiation; $\tau_{1/2}$ is the time of dark relaxation of the photoinduced form when the optical density changes by half.

Scheme 13.



X = O, S, Se.

Scheme 14.



Negative photochromism is also manifested by the hybrid dimer compound DC 1, in which the 1,1′-binaphthyl fragment is bound with two diphenylimidazolyl fragments [33, 34]. The basis of photochromic transformations is the reversible dimerization of these compounds with the participation of short-lived radical intermediate photoproducts (Scheme 15).

This compound in benzene is characterized by an absorption band in the visible region of the spectrum with a maximum at 500 nm, which disappears when irradiated with visible light (Fig. 16). The color is restored within 20 min.

In addition to the above-mentioned spiro compounds (spiropyranes and spirooxazines), negative photochromism was found for metacyclofane-dienedihydropyrenes (DP) (Scheme 16) [35–37]. Compounds of this type DP 1 are characterized by an intense green color, which disappears when irradiated with visible light (Fig. 17) [37].

The analysis of the scientific and technical literature data shows that photochromic organic compounds and

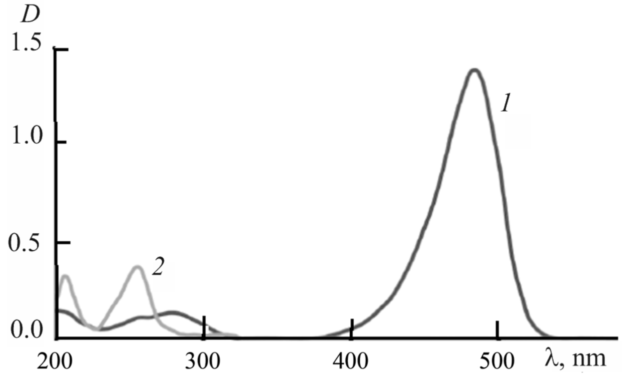


Fig. 13. Absorption spectra of the compounds SC 1 in water before (*1*) and after irradiation with visible light (*2*).

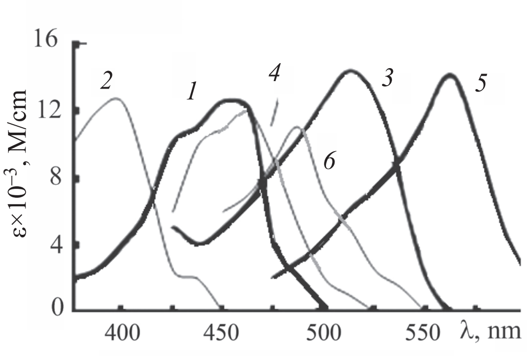
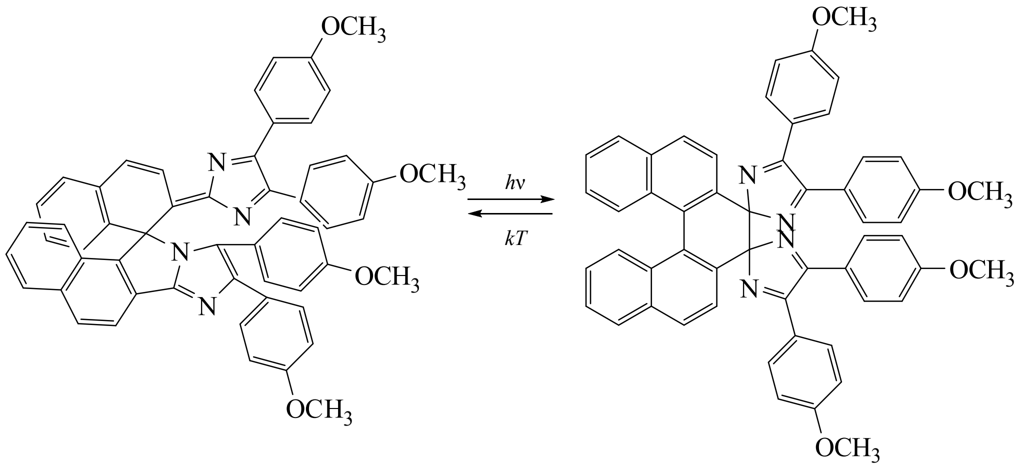


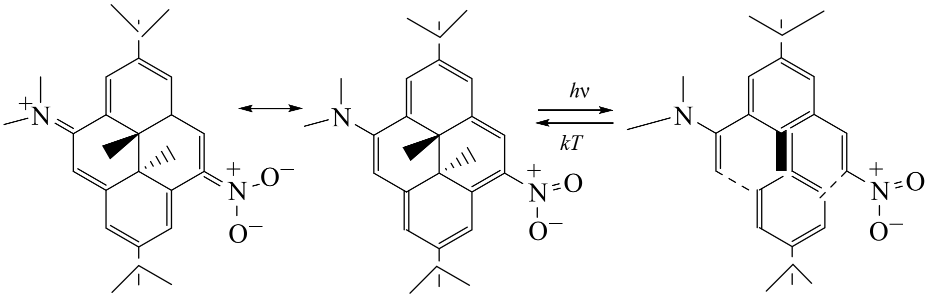
Fig. 14. The absorption spectra of *trans*- (*1*, *3*, *5*) and *cis*- (*2*, *4*, *6*) forms of 3,3′-dioxo-4,4,4′,4′-tetramethyl-2,2′-thioanilidene (*1*, *2*), 6,6′-diethoxythioindigo (*3*, *4*) and selenoindigo (*5*, *6*) in benzene ($c = 1\times10^{-5}$ M).

Scheme 15.



DC 1

Scheme 16.



DP 1

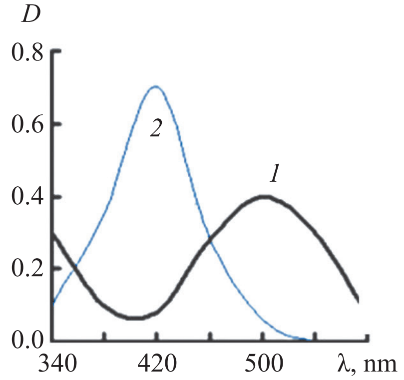


Fig. 15. Absorption spectra of the initial (*1*) and photoinduced (*2*) forms of triphenylformazane in benzene.

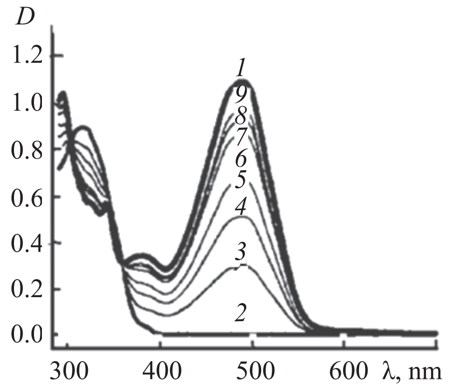


Fig. 16. Absorption spectra of the compound DC 1 in benzene before (*1*), after irradiation with visible light (*2*) and subsequent spontaneous staining (*2–9*)

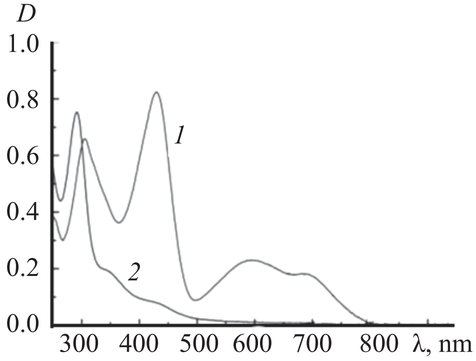


Fig. 17. The absorption spectra of the compound DP 1 in acetonitrile (*1*) and after irradiation with visible and infrared light (*2*).

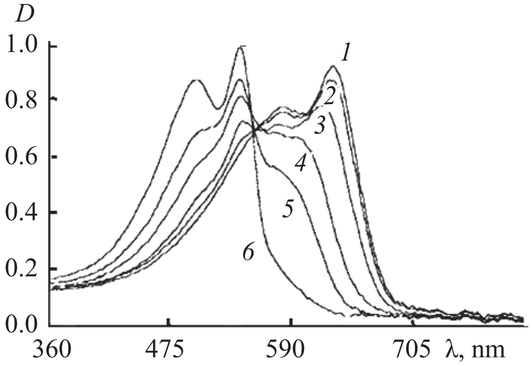


Fig. 18. The absorption spectra of the polydiacetylene PDA 1 film at temperatures, °C: 23.7 (*1*), 29.7 (*2*), 45.4 (*3*), 53.4 (*4*), 60.9 (*5*), and 67.9 (*6*).

systems based on them can provide the development of photochromic coatings with negative photochromism with any given color change according to their spectral-kinetic properties. The disadvantages of photochromic materials include the temperature dependence of the speed characteristics of photochromic transformations, which complicates the problem of color change in case of a sudden change in illumination conditions. To eliminate this disadvantage, photochromic coatings should have the technical possibility of heating.

Thermochromic Substances and Systems

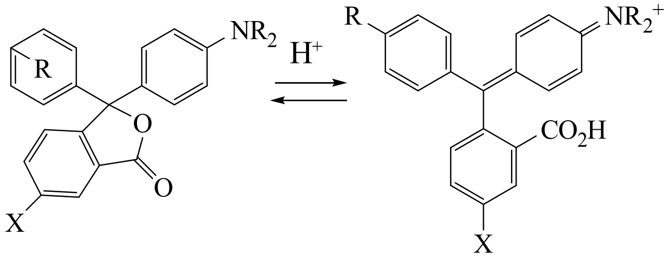
The phenomenon of thermochromism consisting in a reversible change in color when the temperature of a substance changes, is inherent to organic, elemental-organic and inorganic substances. The temperature range of color changes depends on the nature of thermochromic substances and systems based on them. Their use is only limited by the degradation temperature (usually less than 300°C), at which thermochromic properties are lost.

The use of thermochromic substances in chameleon-type coatings is based on their property to reversibly change color when heated. In terms of technical capabilities, they are inferior to photochromic coatings, since their use involves the use of heating elements. However, they are superior in terms of availability. Currently, a large range of thermochromic microcapsules of various colors with different response temperatures is produced abroad, providing a rapid change in color when the temperature changes [40].

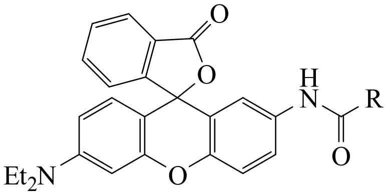
The greatest attention is paid to the development of microcapsulated thermochromic systems based on leuco dyes [38, 39]. Such thermochromic systems usually consist of three components: a pH-sensitive dye, a proton donor that plays the role of a color developer, and a hydrophobic non-volatile solvent.

The process of thermochromic color change is based on the acid dependence of the absorption spectrum of dyes (Scheme 17).

Scheme 17.



Scheme 18.



BF 1: R = 2-$AcOC_6H_4$; BF 2: R = 2-HOC_6H_4; BF 3: R = C_6H_{15}.

To achieve the desired effect, these components are mixed in strictly defined ratios and usually microcapsulated to protect the balanced system during subsequent manipulations in different fields of application. The pH-sensitive dyes mentioned, often called leuco-dyes, usually belong to the class of spirolactones (including diarylphthalides) or fluorans. The disclosure of the colorless lactones cycle during protonation by means of color developers such as weak acids leads to the appearance of color. Compounds of different classes can be used as color developers, however, phenols and, in particular, Bisphenol A, which provides bright colors and sharp contrast when changing colors, remain the most popular and practically important. As solvents, fatty acids with a low melting point, amides and alcohols such as stearyl alcohol are most often used. In the production of such pigments, the selected color-forming agent, developer and solvent are fused together and then cooled to obtain a colored pigment. An important stage is the microcapsulation of the composition, and it is carried out according to standard methods of coacervation or interfacial polymerization [40]. The thermochromic formulations obtained in this way are characterized by the following advantages:

—color change occurs within just a few degrees;

—color transition temperature can be changed by selecting a solvent;

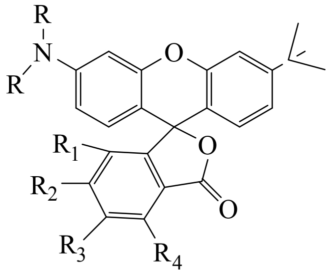
—wide range of color characteristics from the gamut, covering yellow, red, blue, green and black.

The pigment is colored in the solid form of the material, since in this state there is an interaction between the color-forming agent and the developer. Melting of the composition (solvent) disrupts this interaction, which manifests itself in a negative thermochromic effect with color loss.

As a result of studying such systems, the following rules for optimizing their reversible thermochromic properties are formulated: "high color contrast, low equilibrium color density and fast discoloration rates. This can be achieved by selecting such developer-solvent combinations that reveal the presence of a strong affinity for each other and, preferably, the ability to form binary compounds in the solid state" [41]. Usually, when heated, a color transition from a colored to a colorless state is observed. However, due to the careful selection of a pH-sensitive dye, it is also possible to achieve the transition from one color to another. The thermochromic pigments mixtures with different melting temperatures can be also used. In such systems, as one of the components loses its color during melting, the color of the composition will change to the color of another component remaining in the colored form with a higher melting point.

Depending on the component composition, the colors and the discoloration temperature can vary significantly [42-49]. The study results of the conductive tissues samples with microcapsules based on commercial leuco dyes (Americos thermochromic red (T_{act} = 27 °C), Americos thermochromic yellow (T_{act} = 25 °C), Americos thermochromic light blue (T_{act} = 27 °C), Americos thermochromic green (T_{act} = 26 °C)) showed that at a voltage E = 10 V, the staining time (or the temperature increase to the T_{act} value) was no more than 50 s [50]. At the same time, samples of camouflage fabrics were created not only with a mixture of thermochromic compounds, but also with the use of conventional dyes, which made it possible to expand the range of colors that reflect the surrounding landscape. Graphite was used to increase the thermal conductivity of thermochromic fabrics [51]. Using polymer compositions containing thermochromic compounds of blue and orange initial coloring, as well as a natural dye – turmeric and graphite, samples of camouflage coatings were created by means of

Scheme 19.



FL

screen printing. The color change of the thermochromic fabric sample is carried out at voltages not lower than 7 V at a current of 570 mA.

To obtain thermochromic tissues, microcapsulated compositions based on benzofluoranes BF 1–BF 3 in combination with bisphenol **A** as a color developer and octadecanol as a solvent were also used [52] (Scheme 18).

Such color changes are manifested by microcapsulated systems based on *tert*-butyl-substituted fluorans FL [53] (Scheme 19).

The new synthesized fluorans with hydrobenzaldehyde substituents make it possible to create microcapsulated systems in methyl stearate without using a developing agent (Scheme 20), which simplifies the technology for obtaining thermochromic materials [54].

To obtain thermochromic microcapsules, 3,3-bis-(4-dimethylaminophenyl)-6-dimethylaminophthalimide, 2,2-bis(4-hydroxyphenyl)propane were used in a mixture with aliphatic alcohols (Scheme 21) [55].

The existing range of thermochromic systems makes it possible to create microcapsulated materials with various color changes [56].

Using leuco dyes of different structures, it is possible to obtain fabrics with different color rendition, which is important for the development of coatings that completely discolor when heated [57].

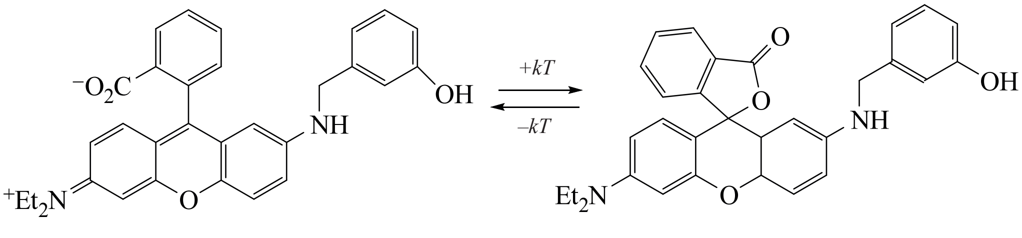
To obtain an electrically controlled thermochromic fabric with a layer of microcapsules containing a thermochromic substance, it is proposed to use fibers made of electrically conductive poly-3,4-ethylenedioxythiophene (PEDOT) [58].

Instead of thermochromic microcapsules, silicon dioxide (SiO_2) nanoparticles functionalized with thermochromic dyes can be used to produce thermochromic tissues [59].

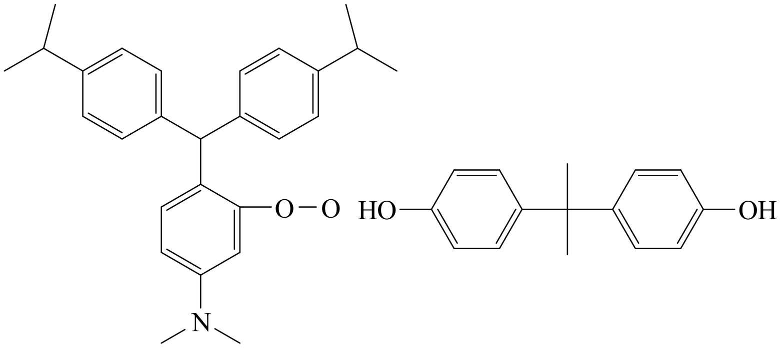
Excellent thermochromic properties are shown by polydiacetylenes PDA 1 and PDA 2 (Fig. 18) [60–63].

Thermochromic substances also include liquid crystal substances [64]. To create thermochromic materials, we use cholesteric liquid crystals (LC), as well as a mixture of cholesteric and nematic LC. Unlike most thermochromic systems, which require a large amount of energy to

Scheme 20.



Scheme 21.



change color, LCD systems change color at temperatures of 5–15°C from 1°C. However, LCD thermochromic materials are characterized by low color saturation and are quite expensive.

The analysis of the data of scientific and technical literature in the field of development of thermochromic systems shows that the most acceptable properties are thermochromic systems based on organic compounds. In a microcapsulated form, such systems allow you to create thermochromic fabrics suitable for creating chameleon-type coatings.

CONCLUSIONS

Photo- and thermochromic substances and systems based on them can be successfully used for the development of coatings of the chameleon type with controlled dynamic color change. The results were obtained, in each of these fields, indicating the possibility of developing coatings with the required controlled spectral characteristics in the visible spectrum range for their use in the summer, spring, winter and autumn seasons for almost any geographical area.

Analysis of the study results of photochromic substances and systems shows that only photochromic systems with negative photochromism can be used in the development of chameleon-type coatings. Such materials are discolored under intense solar radiation and colored when the intensity of solar radiation decreases. In this case, the color intensity changes automatically with a change in illumination.

The fastest solution to the problem of creating chameleon-type coatings with the required properties is possible using thermochromic substances and systems based on them that change color with a slight (5–20°C) temperature change.

To improve the operational and optical characteristics of chameleon-type coatings, the joint use of thermochromic and photochromic substances is of interest.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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