Specific Features of Photodestruction and Photostabilization of Dyed Textile Materials

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The present paper is a brief review of some basic problems linked with the analysis of lightageing regularities of dyed textile materials. Finished textile materials are as a rule a complicated composition from fibreforming polymers, dyestaffs (or their mixtures) and special preparation giving a set of predetermined consumer properties to the dyed polymer material (finishes). These components have different lightfastness and, besides, can differently influence on lightfastness of each other.

KEYWORDS: Photodegradation, pigments, textile materials, chemical composition, physical structure, quantum yields

Many articles of everyday and special use containing both basic and auxiliary textile materials, are being exposed under conditions of prolonged and intensive exposing to light, or natural illumination (outerwear, curtains, blind, upholstery fabrics, swimwear and bathing accessories, tents, shelters, sails, ropes, parachutes, etc.). Most often these articles and materials are being exposed not only to light or light–weather but in combination with other factors, e.g. mechanical, biological, chemical and other effects.

For most of the above-mentioned textiles and articles the effect of light and light–weather, i.e. photoageing, is predominant. Hence the technical and economic significance of the lightstabilization problem as well as the lightfastness evaluation of dyed textiles is obvious.

Lightageing and lightstabilization problems, lightfastness evaluation of textiles are analysed both in this country and abroad within a number of scientific schools. In the Soviet Union these problems are tackled in the Academy of Sciences, in higher school establishments and branch research institutes. Among foreign schools, those of Great Britain, USA, the FRG, Switzerland and Hungary should be given special mention. Practical aspects of the lightageing problem for textiles (dyed polymer materials, in particular) include two independent tasks relating to lightstabilization and lightfastness evaluation. Both of these practical tasks, with their specific features of practical and theoretical nature, are based on photochemistry and photophysics of the lightageing process as the key to their solution.

Principle ageing regularities of polymer textiles, including dyed polymers, are given a detailed consideration in Soviet and foreign monographs.[1-5] Here we will give a brief review of some basic problems linked with the analysis of lightageing regularities of dyed textile materials. It should be noted that many of these problems are common for dye and polymer photodestruction, whereas some of them are specific namely for lightageing of dyed textiles.

Finished textile materials are as a rule a complicated composition from fibre-forming polymers, dyestaffs (or their mixtures) and special preparations giving a set of predetermined consumer properties to the dyed polymer material (finishes).

These components have different lightfastness, fibre lightfastness being most frequently higher than that of dyes and finishes. Some combinations of fibres, dyes and finishes are certainly falling out of this line, but the general regularity is in most cases preserved, which leads to two practical conclusions.:

1) Fibre–dye–finish combinations should be matched from components with similar lightfastness values.

2) Whenever the above-said combination is impossible to obtain, attempts should be made to increase dye and finish lightfastness.

An exclusion from this is, for instance, polyamide fibres, whose lightfastness is so low that being exposed to intensive light and light–weather the dyed polyamide materials lose their strength characteristics much sooner than the brightness of the dye layer, produced with the majority of disperse, acid or reactive dyestaffs.

Below we will look more closely into the lightfastness of all the enumerated components.

Fibres

According to their lightfastness all the fibres can be put in series with regard to exposition conditions (light only, light–weather) and addon content (matted, non-matted). The extremities will be manifested by polyacrilonitrile (most lightfast), and polyamide and silk fibres.

Different lightfastness of fibres is determined by at least 3 factors:

– the chemical composition of a fibre-forming polymer;

– The nature and content of admixtures in the fibre as a technical product;

– physical structure, micro- and macrostructure of the fibre.

Evidently, the fibre-forming polymers of different chemical composition may have a greatly varying physical-chemical activity. However, even if the fibre-forming polymer itself is quite inactive photochemically, the admixtures in the technical product may considerably affect its lightfastness. This refers, for example, to polyamide as some of its chains contain α-keto-imide groups, which

are photoactive and lead to the process by the radical mechanism. Similarly, the fibrematting addons (e.g. titanium dioxide) with definite physical structure, in the atanose form, considerably increases photodestruction of many fibres. On the other hand, lightstabilizers, purposefully introduced into the fibrous material as addons, ensure a dramatic rise of fibre lightfastness.

It should be noted that in terms of their mass content (less than 5–10%) dyestaffs and finishes can also be considered as admixtures, which often are not inert fibre fillers as they raise or lower its lightfastness. Besides, the fibre, its physical structure and chemical composition influence both the dye lightfastness and the finishing effect. Thus the majority of disperse dyes, for instance, have a higher (by 1–2 points) lightfastness on polyester rather than on polyamide fibres; some vat anthraquinone and polycycloquinone dyes greatly accelerate photo-destruction cellulose and polyamide fibres.

Dyestaffs

Lightfastness of dyestaffs or, more correctly, colour of textile materials is determined by a number of factors including the physical state of the dye, the degree of its aggregation, distribution in the fibre, etc., the principal one being the chemical composition of the dye which influence its spectral characteristics and photochemical properties. Since the chemical composition of the dye determines its lightfastness, the proper choice of a class or a definite dyestaff for dyeing a textile material of certain end-use is a point of great significance for textile production.

Generally the series of dyestaffs, in terms of their lightfastness, can be represented as follows (in technical classification): vat > reactive, acid, dis-perse, cation (anthraquinone) > reactive, direct, acid, disperse, cation, insoluble (azo-) > cation (with a distributed positive charge).

Dye stability depends not only on the photochemical activity of the molecule, but also on its ability to reversible photochemical transformations. Dyestaffs based on anthraquinone and polycycloquinone rings possess greater stability (undergo a reversible photoreduction) than azodyes (irreversible photoreduction or photooxidation).

Finishes

The effect of numerous finishing agents on dyes lightfastness and particularly on fibres themselves has been the subject of very few investigations. There are systematic studies (the FRG, the Soviet Union, Hungary) only on the minor problem of low crease finishers' influence on the lightfastness of reactive and direct dyes in the treatment of N-methylole derivatives of ethylenurea. This is caused by the fact that most of these finishes considerably affect the lightfastness of dye layers, particularly those applied with reactive dyes having the azochro-maphore structure.

In the collaboration of Moscow Textile Institute and Budapest Technological University it is shown that the photosensitizing of dyes destruction with

preparations of the above-said, type is connected with the growing share of dye molecules which are destroyed by the radical mechanism. Understanding of finish interaction in terms of its effect on dyes and fibres lightfastness will simplify selection of fibre–dyestaff–finish compositions compatible in their lightfastness.

Below we give more detailed analysis of sensitizing effect of some vat polycycloquinone dyes, particularly, yellow and orange ones, on photodegradation of cellulose dyed with them. This phenomena is believed to be based on reversible photoreduction process—dark oxidation involving a fibre-forming polymer, which is the hydrogen donor. Dye photoreduction products are registred to their absorbtion spectra, which differ from those of original dyes.[6] However, it appeared impossible to detect the presence of photoreduced forms in absorbtion spectra for many dyes-sensitizing (e.g., for vat gold-yellow GKh or pyrantron) whereas for vat dyes which are inert regarding cellulose destruction, photoreduction was easily detected in their adsorbtion spectra (dye bright-green S). The said discrepancies prove doubtful a predominant role of dye photoreduction in the processes of accelerated of dyed cellulose photodestruction. As an alternative of the mechanism discussed above the determined role in photo-destruction processes was hypothetically attributed to the vat dye capacity to generate singlet oxygen ($^1O_2$) with photoirradiation. In fact, we revealed this capacity in a number of vat dyes[7] and therewith a correlation between quantum yield of $^1O_2$ generation by the vat dye and its ability to destroy the fibre (cellulose) (Table I).

However, as is known from the literature, the cellulose not containing even

TABLE I

Quantum yields of dye-photosensitized formation of $^1O_2$ in CCl_4 (marked *) and $CDCl_3$ (marked **), residual tensile strength values P/P_0, % after 3-month irradiation, and ability of photoreduction

N	Technical and chemical designation of the dye	(± 10%)	Residual strength P/P_0, %	Ability of photoreduction
1.	Vat gold-yellow GKh (2,3,7,8-dibenzpyrenequinone)	0.8* 0.65**	56	easily photoreduced
2.	Vat gold-yellow KKh (4,9-dibrom-2,3,7,8-dibenzpyrene-1,6-quinone)	0.8*	61	easily photoreduced
3.	Kaledon gold-orange G (pyrantron)	0.8**	55	easily photoreduced
4.	Vat bright-green G (dibrom-16,17-dimethoxyviolantron)	0.02**	81	not easily photoreduced
5.	Vat bright-violet K (6,15-dichorisoviolantron)	0.2*	73	not easily photoreduced
6.	Vat dark-blue O (violantron)	0.03	80	not easily photoreduced
7.	Without dye	—	87	not easily photoreduced

C═C links is not referred to polymer materials easily oxidated with singlet oxygen.[8] Therefore, inspite of this correlation present, the determinative role of the latter mechanism (involving $^1O_2$) was also believed unlikely to occur.

Here we suggest a new approach to this problem, worked out in collaboration with Karpov Institute of Physical Chemistry, which will provide a better understanding of the chemism of occuring photoprocesses. It is suggested that the photochemical transformations of the dyestaff eventually causing the cellulose photodestruction be considered with regard to the dye state in a substrate, i.e., photochemical transformations of molecular (M) and associated (A) dye forms should be analysed separately. This problem is easily solved spectroscopically, when the absorbtion spectra of M- and A-forms are distanced considerably in their wavelengths, if they overlap, additional research is needed.

In the course of comparative studies of photochemical behaviour of some vat polycycloquinone dyes, both reactive and non-reactive with regard to cellulose destruction (Table I). Taking into account that the vat dyes mentioned above are brightly fluorescent in solutions in organic solvents, we used a sequence of spectral-luminescent methods of reseach (we studied absorbtion spectra of secondary derivatives from absorbtion spectra, fluorescence spectra and fluorescence excitation spectra). We stated the presence of the dye in M-form in the dyed sample (cellulose film) by comparison of its absorbtion and fluorescence spectra with the spectra of the same sample put in a medium where it can exist either in M-form or in A-form. These media are, on the one hand, organic solvents (in very diluted solutions the dyes are molecularly dispersed), on the other hand, water which is a medium where the dye is completely associated.

It was found that luminescence spectra of yellow dyes in M- and A-form display a mutual shift exceeding 100 nm, whereas the green, violet and blue dyes possess luminescence only if they are in the M-form. This observation greatly facilitated the identification of M-form and A-form of dyes in a sample.

Using this qualitation method of dye state evaluation, based on the comparative analysis of luminescent and spectrophotometric data, we showed that within a broad concentration range ($c > 0.3$–$24 \, g/kg$) in dyed samples where the overwhelming part of the dye is associated, practically a small portion of the dye is present in the M-form, which is easily detected from the fluorescence spectrum.[8]

Applying the reliable identification techniques for M- and A-forms of dyes in a dyed substrate, we could demonstrate that all the yellow dyestaffs in M-form subjected to analysis are readily reduced to the leikoform by visible light. There occurs the "burn-up" effect of fluorescence, i.e. the increase of fluorescence intensivity and the transformation of the molecular fluorescence line—instead of the initial M-fluorescence lines more intensive, batochromatically shifted lines of photoreduction product fluorescence appear. Herewith, absorbtion spectra remain practically the same (due to small M-form content in a sample its absorbtion spectrum, as well as the absorbtion spectrum of its photoreduction product are completely overlapped by a wide blurred line of A-form absorbtion), dye aggregates display high lightfastnesss.[9]

The photoreduction process is reversible, in the course of storing irradiated

dyed cellulose films the photoreduced form is gradually oxidized. The reverse reaction is particularly speeded up with the moistening films.

For the violet, blue and green dyes not belonging to the dyesphotosensitizers, under the said condition no traces of the photoreduction reaction are detected.

From the abovesaid it becomes clear that the source of controversy in data obtained by different authors[10] lies in their neglecting the dye state in the cellulose material. In spectral analysis it is necessary to draw a sharp distinction between peculiarities in photochemical behaviour of M- and A-forms.

Thus, we may suppose that only those vat dyes act as photosensitizers of cellulose destruction which are effectively photoreduced due to separation of a hydrogen atom from cellulose and are capable to generate singlet oxygen with quantum yields approaching 1. Hereby the molecular form of vat dyes engaged in the photodestruction process of cellulose may act as a destruction catalyst.

Dyestaffs may make both sensitizing and stabilizing effects on polymer photodestruction. The stabilizing effect of dyes is found in different textile polymer systems, such as reactive dyes—cellulose; acid, disperse dyes— polyamide and some others.

The greatest interest is attached to lightfast dye-polyamide systems, as articles from polyamide materials, widely used in the national economy have a serious disadvantage of low lightfastness. Polyamide articles of many types are subjected to dyeing which makes light-stabilizing with dyes economically profitable.

We investigated three possible mechanisms of increasing lightfastness of polyamide with dyes: UV-screening, quenching of excitated polymer states, inhibition of radical reactions.

It was found that the light-stabilizing effect of disperse dyes considerably exceeds the effect of screening photochemically active light with dyes.[11]

To provide studing possibilities the action of dyes as quenchers of photochemically active excited polymers states the effect of dyes on the luminescence intensivity of polyamide was studies, and the latter being characterized with λ_{max} of excitation and fluorescence 365 and 445 nm respectively.

In the presence of disperse dyes the luminescence intensity of polyamide decreases to a certain degree what is connected with the screening effect of dyes, as the majority of dyestaffs effectively absorb both the light excitation luminescence and the polymer's own luminescence. Consequently, screening coefficients at $\lambda = 365$ and 445 nm were introduced into the obtained dependences of relative polyamide luminescence on dye concentrations.

Table II sums up the results of lightfastness testing of capron cloth, dyed with disperse dyes (~3% of polymer weight). Samples lightfastness was derived from their residual tensile strength after a month-long insolation under natural conditions. Comparison of data from Table II and the dependences of relative luminescence intensivity of polyamide film, dyed with different dispersed dyes, on the dye concentration shows that a considerable stabilizing effect comes from the dyes which are effective in the quenching of polyamide luminescence.

A closer look into the link between quenching and stabilizing effects of dyes was taken with 4 dyes as examples. Table III shows the results of open-air testing lightfastness of polyamide cloth, which was evaluated from the amount of residual

TABLE II

Influence of disperse dyes on lightfastness of capron cloth

N	Designation of the dye	Residual strength P/P_0, %	N	Designation of the dye	Residual strength P/P_0, %
1.	Bright-orange G	33	4.	Bordo	70
2.	Yellow fast 4K	79	5.	Yellow Z	77
3.	Violet K	71	6.	Yellow MP	80
			7.	Without dye	36

tensile strength P/P_0 after a half-month and a month-long irradiation, and the value assumed as the measure of luminescence quenching efficiency $(1 - I/I_0)$. Luminescence measurements were conducted on the polyamide film dyed simultaneously with the cloth.

As is seen from Table III, a sufficiently close correlation exists between the luminescence quenching efficiency of polyamide and the stabilizing effect of the investigated dyes. However, the quantative evaluation of final data is complicated due to the fact that the consideration of light-stabilizing effects of dyes necessitates the lightfastness of the dye itself to be taken into account (i.e. decreasing its concentration during samples lightageing).

The obtained data agree with found in literature,[12] according to which the

TABLE III

N	Designation of the disperse dye	Dye concentration, mol/kg	Residual strength, P/P_0, % Irradiation time, month 0.5	1	Efficiency of quenching $(1 - I/I_0)$, %
1.	Yellow MP	$1.4 \cdot 10^{-3}$	62	44	63
	Yellow MP	$6.7 \cdot 10^{-3}$	75	55	93
	Yellow MP	$10.0 \cdot 10^{-3}$	76	57	87
	Yellow MP	$19.5 \cdot 10^{-3}$	73	59	97
2.	Yellow Z	$1.0 \cdot 10^{-2}$	67	63	67
	Yellow Z	$3.7 \cdot 10^{-2}$	76	67	81
	Yellow Z	$9.7 \cdot 10^{-3}$	85	76	96
	Yellow Z	$10.7 \cdot 10^{-2}$	87	74	86
3.	Violet K	$0.7 \cdot 10^{-2}$	57	40	37
	Violet K	$2.5 \cdot 10^{-2}$	71	49	79
	Violet K	$2.3 \cdot 10^{-2}$	75	57	80
	Violet K	$3.8 \cdot 10^{-2}$	74	58	89
4.	Violet 2B	$0.7 \cdot 10^{-2}$	65	44	56
	Violet 2B	$2.9 \cdot 10^{-2}$	71	61	56
	Violet 2B	$4.7 \cdot 10^{-2}$	79	64	72
	Violet 2B	$5.4 \cdot 10^{-2}$	81	61	75
5.	Without dye	—	45	26	—

initiation stage of radical transformations involves the intermediate products, responsible for polyamide fluorescence, this product have allegedly the α-ketoimide structure. Therefore, the observed intensity decreasing in polyamide luminescence in the presence of dyes may be linked with quenching the photochemically active state of the destruction photoinitiator.

In the paper[13] a notion of the effective volume of dye distribution zones against the polyamide luminescence centers was introduced. It was also shown that the dyes stabilizing polyamide are mainly localized in the same zones of the polymer matrix there the polyamide luminescence centers are concentrated. Dye concentration in localization zones of initiating centres may by 2 orders of magnitude exceed the average dye concentration meant for the total sample volume.

On the basis of such studies we can suggest a method of preliminary selection of lightstabilizing polyamide dyestaffs based on their efficience of quenching polyamide luminescence. According to this method, luminescence intensivitiy of dyed and undyed samples is determined and the quenching efficience is calculated.[14]

The described systems are vat dyes-cellulose and dyed polyamide, which are the few dyed textile materials with their use-period depending on the life of the polymer. In the most cases, as mentioned before, the factor determining the use of a dyed textile material is the dye lightfastness.

Principal ways of increasing dye lightfastness of textile polymer materials which are determined by the photodestruction mechanism are given a detailed consideration elsewhere.[15] There are UV-screening, quenching of excitation states and deactivation of chemically active particles.

However, dyed textiles have their specific features complicating the use of stabilizers, acting by the said mechanism. Primarily due to the dispersion ability of the fibre the visual dye-fading effect is caused by the dye destruction in some surface layer. It is due to this regularity that the use of UV-absorbers for increasing dye lightfastness leads to the notable effect only on synthetic fabrics having no matting agent. Besides, the additional treatment of the textile material changing the optical characteristics of the fibre can evidently change the dye lightfastness as well (in case of its visual evaluation accepted in the textile industry). Thus, the treatment of cellulose textile materials dyed with reactive azodyes and vat dyes, concentrated alkaline solutions (the mercerisation process) increases dye lightfastness by 1–2 without any notable effect on physical-chemical properties of dyes.

The main property of the textile materials is that, different from the majority of polymers, the introduction of both the dye and other addons is accomplished from solutions into the finished fibre or fabric. In this case the main factor is the mutual distribution of the dye and the stabilizer in the polymer film.

In a collaboration of the Institute of Chemical Physics of the USSR Academy of Sciences it was shown that the volume share of distribution zones of dye molecules constitutes ~0.7% for cellulose hydrate and ~2% for polyamide, against the volume of whole polymer matrix. It was also found that the stabilizers belonging to the class of metal containing compounds (e.g., dibutylditiocarbam-

ates of metals (DBTC)) are localized in the same zones of a polymer matrix. This reveals the principal possibility of using stabilizers which act to the mechanism of quenching excited dyes states for increasing dye lightfastness.

The correlation of results of testing lightfastness of film and fabric samples, treated with different metal containing compounds, with the results of luminescence testing proved this to be another case of possible use of the luminescence method for screening potential stabilizers. It should be stressed that the method is applicable for any stabilizers which can quench excited dye states.

At present good results (1–2 points) are obtained using stabilizing addons in different systems: metal-containing stabilizers for reactive, sulphuric, vat and soluble vat dyes on cellulose materials, sterically hindered piperidines and stable nitroxyl radicals for direct and disperse dyes on viscose and polyamide fabrics, etc.

Choosing stabilizing addons should also be done with regard to the effect of finishing agents. Thus, increasing dye lightfastness with reactive dyes by 1.5 points is achieved by application of nickel DBTC. However, for dyed finished fabric a similar increase can be achieved only with the mixture of stabilizers containing, besides nickel DBTC, inhibitors of radical processes.

Using stabilizers for increasing lightfastness of dyed textile materials gives rise to more problems, e.g. introduction of stabilizers insoluble in water, attachment of stabilizers soluble in water to the fabric and so on. By present some of these problems have been partially solved and, for their purely, technological nature, may be covered by other kinds of reports.

In conclusion, it may be noted that presently a general photophysical and photochemical understanding of lightfastness of dyed textile materials is developed. The dyed textile material is destroyed to the laws of the solid polymer, with considerable manifestation thereby of specific features of these materials as composites containing the polymer (90%), the dye and the finish.

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