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From Murex Purpura to Sensory Photochromic Textiles

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1. Introduction

Throughout history the function and the original role of the textile changed very little. One could only think of only few generations of textiles that would bear significant differences when compared one to another. Textiles were to provide the necessary shielding against climatic conditions and only later on in history the sheer design of it became more importance. Nowadays, textile engineers and technologists like to think there is a new generation of textiles emerging. This thinking is supported by new functionalities being added onto textiles in the last few several decades. For this to happen, it was necessary to combine state of the art electronics and newly synthesized organic molecules which would bring the functionality of the textile to another level. Scientists of various research branches working together, looking at issues and solving problems applying multidisciplinary approaches was the right angle of looking at things. Results of this can be seen daily, as textiles are emerging into a new era in which “know how” and “state of the art” have to be combined to give products of highly added values. Producing “highly added value” products can give the leverage to companies of the western world in an ongoing “battle” against massively produced, low quality textiles of mainly eastern origin.

Although, the way to commercialization of many of the ideas of how to upgrade the functionalities of the textile is long, the results may be far greater than the challenges encountered. Often, the answer on how to do it lies in using technologies and knowledge that have been around for centuries. Therefore, this paper will deal with the phenomenon of photochromics, which has first been noticed in 19th century and so far not exploited nearly enough within the realm of textiles (Hepworth et al., 1999). It will cover the historical overview, division of photochromic systems and their synthesis, principals and triggering mechanisms, various fastness property issues and applicability to fibres of different origin (Shuiping et al., 2010). Application methods and state of the art shall be described thoroughly, providing scientific and technological achievements from the relevant literature references (Durr & Bouas-Laurent, 1990).

Group of authors addresses the combination of photochromism phenomenon and textile in general as newly derived system, bearing all the qualities of a sensory material. Within it, molecule of photochromic dye may be observed as “smart”, as it is triggered by a specific and quantifiable physical value. Properly applied, this “smart dye” and adequate textile fibre form a textile sensor capable of sensing and reacting to a particular impulse in a predictable manner (Czarnik, 1995; Van Langehove, 2007).

Described as such, the system bears all the necessary qualities of a smart textile. It is capable of alerting and protecting the wearer from the very specific threat as it has been specifically designed, calibrated and optimized.

From the textile engineer's, namely dyer's point of viewing things, not much has changed. Only the concept of "colour all the time" has changed to "colour at the right time" principle, which may be observed as one of the options of giving leverage to textile companies in search of means and ends of once again reclaiming the leader status on the worldwide market.

2. Chromism

In this text photochromism shall be addressed in a context of products of high added values. These high added values result from functionalities being added, thus moving away from the classical concept of a textile product. The differences between a classical and a high added value product are numerous; production process may be far technologically more demanding, number of functionalities may be increased significantly, technical applicability may be greater and finally the greatest difference may be between the price of production and that of a final product.

When discussing the term photochromic, one should first clear out the term „chromic“. Chromism is a process that induces a reversible colour change of components consisting of a chemical compound. This includes changes on the molecular level like cleavage of the chemical bonds or changes on the level of molecular conformations. In most of the cases, chromism is based on changes occurring inside of the molecule, among electrons. This especially implies „pi“ and „d“ electron positions so that the phenomenon is induced by various outside stimulus bearing the ability of altering electronic density of the compound or a substance (Lee, S. J. et al. 2006; Nakazumi, 1997).

It is well known that many of the natural compounds possess chromic property, while a number of artificial compounds of specifically characterized chromic properties have been synthesized so far (Shibahashi, 2004). Chromism refers to the phenomenon in which colour is the result of a broad spectral interactions among incident light and material (Bamfield, 2001). These interactions may be categorized into following five groups:

- Reversible change in colour
- Absorption and reflection of light
- Absorption of energy followed by the emission of light
- Absorption of light and energy transfer or transformation of energy
- Use (manipulation) of light

These chromic effects are caused by:

- Perycyclic reactions (cyclization, cycloaddition)
- Cis-trans isomerization
- Intermolecular group transfers
- Intermolecular hydrogen transfers
- Dissociation (cleavage of the bonds)
- Electron transfer

Phenomenon including a change in colour of a chemical compound is named according to external stimulus causing the reaction, either physically or chemically (Viková, 2004). Many, but not all of these reactions are reversible. The classification is as follows:

- Photochromism - change in colour of a compound is light induced, based on isomerization among two different molecular structures

- Thermochromism – change in colour of a compound is heat induced, most frequent form of chromism
- Electrochromism – change in colour of a compound is caused by an electrical current. Induced by the acceptance or donation of electrons. The phenomenon is characteristic for compounds of redox active localities, such as metal ions and metal radicals
- Solvatochromism – change in colour of a compound is caused by solvent polarity. Most of the solvatochromic compounds are metallic complexes
- Ionochromism – change in colour of a compound is ion induced
- Halochromism – change in colour of a compound is caused by change in pH
- Tribochromism – change in colour of a compound is mechanically induced (friction)
- Piezochromism – change in colour of a compound is mechanically induced (pressure)
- Mechanochromism – change in colour of a compound is induced by deformation
- Hygrochromism – change in colour of a compound is induced by presence of moisture
- Chemochromism – change in colour of a compound is induced by specific chemical agents i.e. toxic gasses, detergents etc.

Over the past ten years, investigations on thermochromic pigments have gained popularity. These are aimed at obtaining new effects on dyed textile materials. Using a conventional technique of textile printing in combination with thermochromic pigment an intelligent textile is obtained. Intelligence is defined by the ability of the printed textile to change colour in accordance to the presence of an outside stimulus. In this case temperature changes occurring within the close environment of the textile (Karlessi, et al. 2009; Kulčar et al., 2010; Maeda, S. 1999).

As far as quality of the chromic materials goes, it will depend on several parameters:

- Intensity of change in colouring of a compound
- Change in colouring
- Conditions of transition, change
- Dynamics of colour change
- Interval of change
- Simplicity of use
- Reversibility
- Number of colour change cycles it is capable of withstanding
- Fatigue resistance
- Fastness to heat, light, moisture (atmospheric conditions)
- Allergic reactions

3. Photochromism

The phenomenon of photochromism is an analogue to all chromic processes. The change in colour is influenced by light in a reversible way (Fig. 1) (Cheng, 2007). Uncoloured material doesn't absorb light and may only be activated by energetically rich photons of the near UV electromagnetic spectra. Many of the inorganic materials such as copper, mercury, various metal oxides and some minerals exhibit the photochromic phenomenon (Van Gemert, 1999a, b). However, their use is considered inappropriate for textile materials and substrates. Organic molecules such as spiropyrans, spirooxazines and fulgides are suitable for use on textiles (Bouas-Laurent & Dürr 2001).

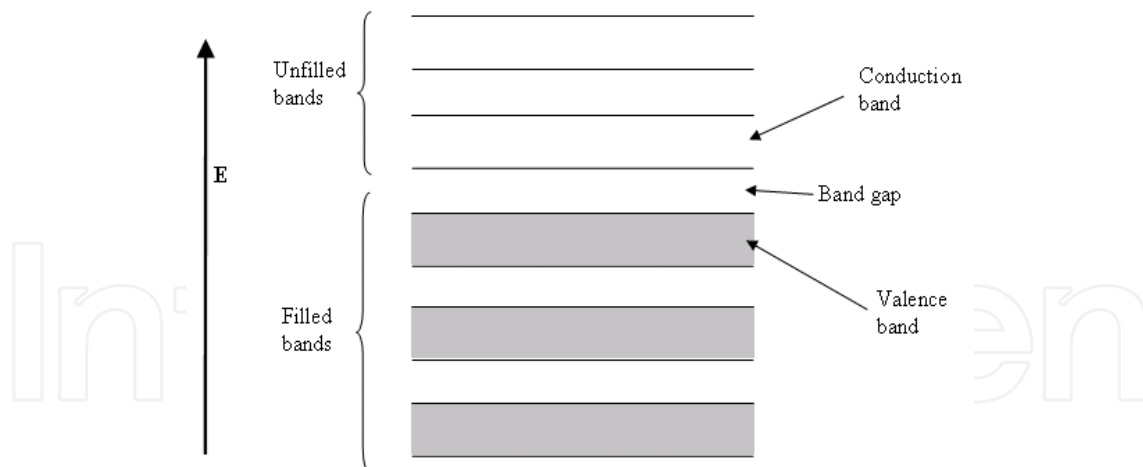


Fig. 1. Mechanism of photochromism

The very principle, the triggering mechanism of photochromism is as follows: chemical compound transitions from form A into a form B, each of them of a specific absorption spectra implying specific colouring of the form, as well. The triggering mechanism is UV light induced (process of activation). As a result of incident UV light, compound changes its colour (Bouas-Laurent & Dürr 2001).



Upon removal of the light source the colouring disappears as the molecule return to their inactivated state i.e. rest state. Deactivation is usually a slower process than activation and hysteretic behavior is noted. In terms of the dynamics of deactivation, visible light spectra and heat increase it, while polar solvents decrease it. Colouring is usually of lower intensity at higher temperatures i.e. reversing proportionate.



By definition, discolouring of the chemical compound caused by UV part of the electromagnetic spectra is called negative photochromism.

There are three different groups of chemical processes on which the transformation of form A into form B is based:

- Trans-cis isomerization
- Variation of conditions under which a metal is oxidized
- Homolytic or heterolytic cleavage of the chemical bond

These reactions have to be reversible in order to be characterized as photochromic. Otherwise, the reaction may be observed as usual metameric reaction (Bouas-Laurent & Dürr 2001).

3.1 Historical overview

The phenomenon of colour changing compound has been noticed and used for millennia. The first known, written documentation is that on Tyrian purple, dating 350 years B.C. i.e. back to the times of Alexander the Great. Dye was obtained from sea snails (*Murex Brandaris* and *Murex Purpura*). Applied onto textile material, the dye is in its uncoloured form and reveals true colouring only after being exposed to sunlight.

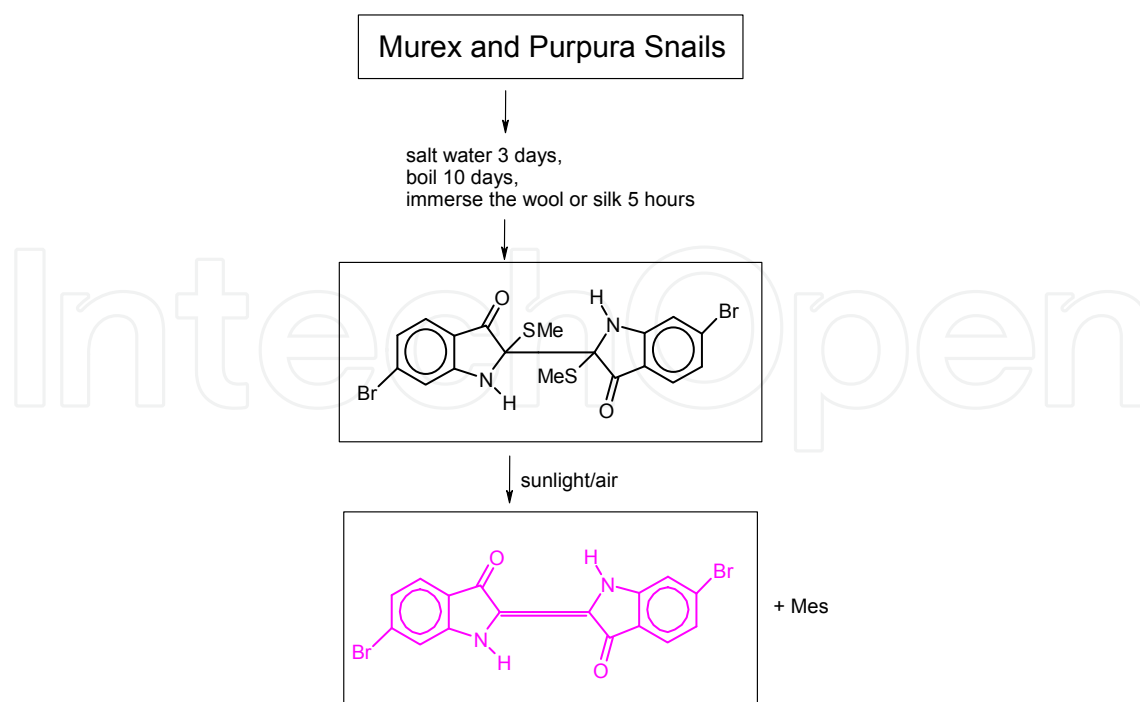


Fig. 2. Preparation of the dye obtained from Murex

Brief description on preparation of the dye and chemical change occurring on molecular level is given in figure 2 (Durr & Bouas-Laurent, 1990).

As far as natural photochromic dyes go, rhodopsin is considered a photosensitive compound of reversible colour capacity. It is present in retina of the eye. Activating mechanism of rhodopsin is of photochromic triggering mechanism. Activated by light, it produces a nerve stimulus, transmitted to the cortex to provide visual perception. Rhodopsin has been discovered inside primitive bacterium, *Halobacterium halobium*. In it, it is responsible of transforming sunlight into energy, which classifies metabolism. Technical applications of rhodopsin, considered as photoswitchable biomaterial include optical data storage and security applications (Hampp, 2005a, b).

Investigations on photochromics on scientific level date back to 19th century. It was J. Fritzsche who first noticed photochromic property of a solution of tetracene, while later on E. Ter Meer noticed it on solid potassium salt of dinitromethane (Bouas-Laurent & Dürr 2001).

3.2 Demands on photochromic system

Ideally, any organic photochromic system should be of following qualities:

1. Development of colour in photochromic systems – in order of being classified a sensor, the dynamics of colour development must be a rapid reaction to source of UV light
2. Return to the rest state (colourless) – the rate of fading of the system has to be controllable and all possible influences, such as influence of heat or sunlight, investigated
3. Wide palette of colours – range of the colours being exhibited as a result of irradiation by UV light should be across the visible range of light
4. Rest state in which colour is not exhibited – the state in which there is no excitement of the electrons, caused by an external stimuli should be as colourless as possible

Photochromic dye appropriately applied onto textile material forms a photochromic system, which in case of fulfilling the abovementioned demand is in fact a sensor (Billah, 2008).

Sensor capable of reacting to UV light of exactly defined spectra and intensity in a pre-programmed, controllable manner. Described as such, system alerts and protects the wearer against negative influence of UV irradiation and classifies the very definition of a “smart textile”. Having fulfilled all of these demands, investigations should be made to find out whether any derived qualities have arisen as a result of applying photochromic molecules onto textile fibres. These qualities may be an increment in UPF (Ultraviolet Protection Factor), a very interesting value for light fabrics in which bear constructional characteristics, such as the type and density of weave cannot provide satisfying UV-R protection. Another interesting quality could be certain antibacterial or antifungal properties added onto textile materials (Bamfield, 2001).

3.3 Classes of photochromic compounds

Photochromic compounds can be divided into five main classes fitting the requirements of an ideal photochromic compounds. These are, as follows:

1. Spiropyrans (Spiroindolinobenzopyrans)
2. Spironaphthoxazines
3. Naphtopyrans (Chromenes)
4. Fulgides
5. Diarylethenes

In terms of applicability to textile fibres, spiropyrans, spironaphthoxazines and chromenes have been found as most suitable considering fatigue, life time and fastness properties. Therefore, this paper will cover physic-chemical properties of these classes of dyes, suitability of use on natural and man-made fibres and several technological techniques of application.

3.4 Spirobenzopyrans

This is a widely studied class of photochromic compounds. They are consisted of a pyran ring, in most cases 2H-1-benzopyran and heterocyclic ring (Fig. 3). Link between the rings is a common spiro group (1.1). The mechanism by which the photochromism occurs is actually cleavage of the carbon-oxygen bond, caused exclusively by irradiation with UV light. The result is a ring-opened coloured species, called “merocyanine” form or MC, which can be cis-(1.2), trans-(1.3) or ortho-quinonoid form 1.4 (Bamfield, 2001, Oda, 2008).

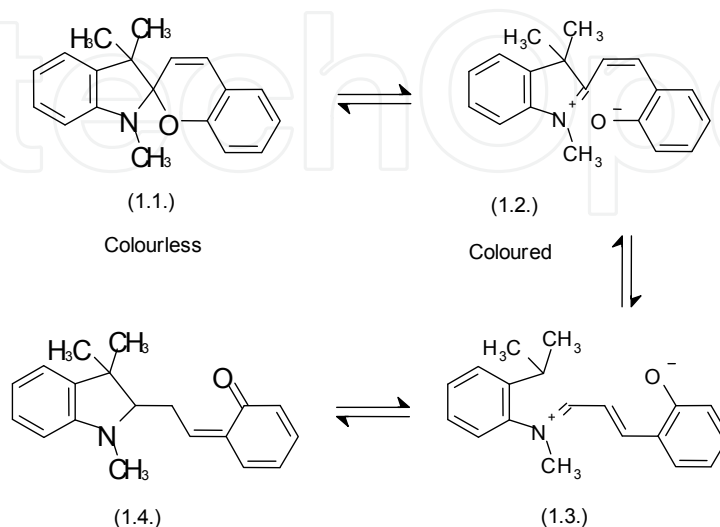


Fig. 3. Spiroindolinobenzopyran and ring opened merocyanine quinonoid form

A large number of substituents are possible for spiropyran ring. Pyran ring is most often substituted benzo or naphthopyran. Heterocyclic component can be varied, as a long list of ring systems is available: indole, benzthiazole, benzoxazole, benzselenazole, quinoline, acridine, phenathridine, benzopyran, naphthopyran, xanthenes, pyrrolidine and thiazolidine.

3.4.1 Synthesis of spiroindolinobenzopyrans

Synthetic pathway to spiroindolinobenzopyrans (Figure 4.) begins with synthesis of Fischer's Base (1.5 - 1.6). Spiroindolino compound is obtained by condensation of Fischer's base (1.6; R=alkyl) with salicylaldehyde (1.7). Another route of synthesis may be with indolinium compound bearing different N-alkyl groups (1.6; R=alkyl) and different ring substituents; chemical reaction of synthesis is shown in Figure 4 by alkylation of a 2-methylindole to obtain (1.8; R=alkyl) (Keum et al., 2007).

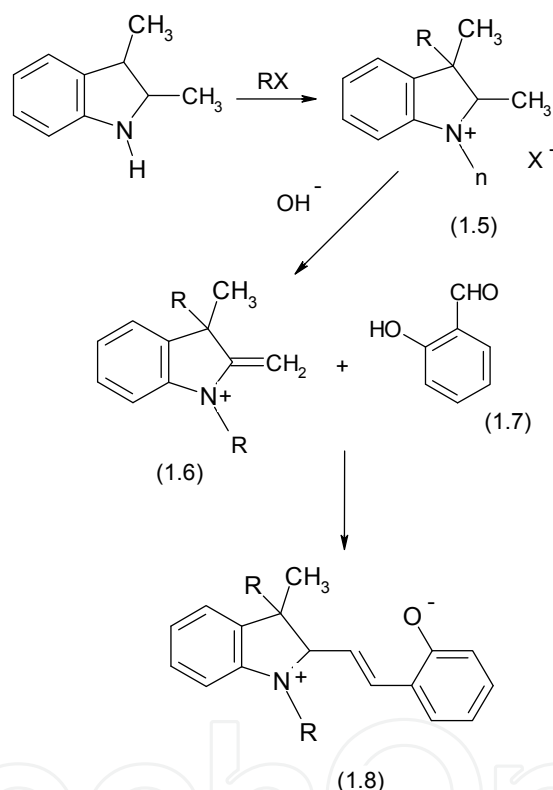


Fig. 4. Synthetic pathway to BIPS and derivatives

6-nitro-1',3',3'-trimethylspiro [2H-1-benzopyran-2,2'-indoline] (6-nitro-BIPS) may be considered to be most studied of all spiro-organic photochromics. Therefore, its synthesis shall be described thoroughly. Description refers to a slightly modified literature method (Inoue et al., 1968; Sivadjian 1968). Fischer's base, 1,3,3-trimethylindole (3,5 g; 0,02 mol) is dissolved in 40 ml of absolute methanol. To this solution, 3,35 g of 2-hydroxy-4-nitrobenzaldehyde (0,02 mol) in small proportions is added over the period of 10-15 minutes. The obtained pink-brown solution is refluxed for 2 h. The reaction mixture is evaporated to a small volume in an air draft. Fine powder is collected by filtration and washed with absolute ethanol and then air-dried. This was recrystallized from boiling n-hexane with a small amount of activated charcoal. Pale yellow microcrystalline powder is obtained (Clarke, 1995).

The route to 1,3,3-trimethyl-spiro[indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine (NISO) is quite similar. Stechiometric compounds of Fischer's base and 1-nitroso-2-naphthol are refluxed in alcohol or toluene for 2-4 hours (Ono and Asada, 1970). Product is collected by filtration, washed with alcohol and air-dried. It is recrystallized from boiling n-hexane with a small amount of activated charcoal. A pale greenish powder was obtained. Both Qiso and BISO can be prepared by similar methods (Hurditch & Kwak, 1987).

3.4.2 Spectral properties of spiroindolinobenzopyrans

MC form of the spiroopyran dyes shows great absorbance in the visible region of the spectrum, typical of merocyanine dyes. This open chain form of the molecule is thermally instable; therefore a rapid scanning absorption spectrophotometer must be used to measure absorption within visible spectrum. Polarity of the solvent plays a key role in preparation of the spiroindolinobenzopyrans as it shifts λ_{\max} of the solutions. Use of non-polar organic solvent is preferable as the compounds aren't water soluble. These classes of compounds are of strongly positive solvatochromic effect, which can be seen from the changing shape of the absorption curve and its position moving hypsochromically as the solvent polarity increases (Suppan & Ghonheim, 1997). In table 1. the changes of λ_{\max} in closed (SP) and open (MC) form of the NISO, as a result of solvent polarity are shown (Keum et al., 2007).

λ_{\max} of the closed SP form of NISO [nm]				λ_{\max} of the open form MC of NISO [nm]	
Ethanol	Methanol	Methylene Chloride	Hexane	Solvent	λ_{\max} [nm]
345	345	346	347	Ethanol	610
317	317	317	319	Acetone	600
297	303	302	303	Toluene	590
				Hexan	560

Table 1. The changes of λ_{\max} in closed (SP) and open (MC) form of the NISO depending on solvent polarity

Also, parent substituents play a key role in λ_{\max} changes of spiroindolinobenzopyran; especially in the 3,6,8-positions. From the table 2. it can be seen that they have the biggest influence on spectral properties of the coloured form of the spiroindolinobenzopyran.

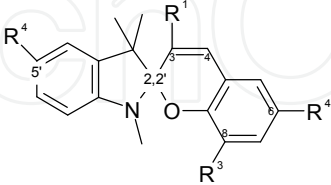
 (1.9)				
R ¹	R ²	R ³	R ⁴	λ_{\max} [nm]
Ph	NO ₂	OCH ₃	H	625
H	NO ₂	OCH ₃	Ph	568
H	OCH ₃	NO ₂	Ph	625
H	NO ₂	H	H	536
H	H	NO ₂	H	544

Table 2. Absorption maximum of the coloured form of substituted BIPS (in ethanol)

3.5 Spiroaphtoxazines

Spiroaphtoxazines are a very interesting group of compounds that can be used on textile fibres (Billah, 2008; Lee, E. et al. 2008). This is because of their increased fatigue and resistance towards photodegradation. Structurally, they are nitrogen containing analogues of the spiropyrans. Photochromic reaction of opening spiroaphtoxazine ring (Son et al. 2007a, b) derivative to its MC form is shown in Figure 5 (Bamfield, 2001).

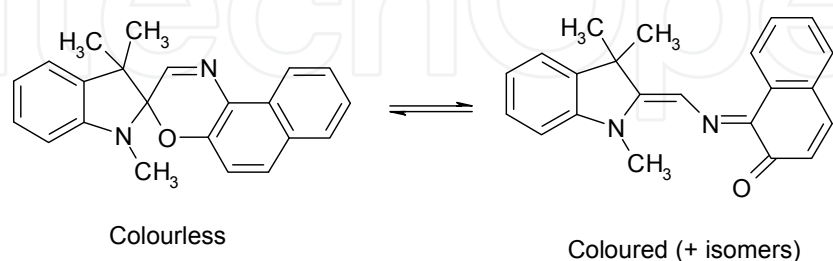


Fig. 5. Spiroaphtoxazine photochromic forms

3.5.1 Synthesis of spiroindolinaphtoxazines

The synthetic pathway to spiroaphtoxazines is based on reaction between 1-hydroxy-2-nitroso bearing aromatic ring and 2-alkylidene heterocycle, such as Fischer's base (1.6; R=H). Naphtoxazines may be chosen from a list of substituents as the stability of nitrosonaphtols starting materials are much more stable than the nitrosophenols required for the parent benzo analogue (Coimbra, 2005). Synthetic pathway of obtaining alkyl substituted naphtoxazines, benzo- and heterobenzo-annulated derivatives is shown in Figure 6. Aqueous solution of corresponding phenolate and sodium nitrate is acidified. Heating the mixture in methanol under reflux gives condensation of nitrosonaphtols with indolines.

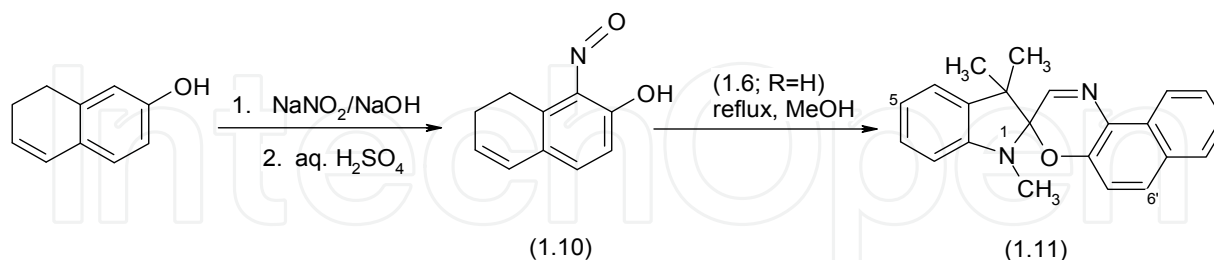


Fig. 6. Synthetic route to spiroindolinaphtoxazine

Most important positions for substitution, affecting colour and fatigue are the 5-position and 6'-position, responsible for both colour properties (expressed as OD-optical density) and molar coefficient coefficient. The substituent on the 1-position has a kinetic effect on the rate of loss of colour back to the rest state. Important thing achieved by described syntheses are overcome colour range issues (550 – 620 nm). Important bearing amino substituents on 6'-position are synthesized from 4-substituted-1-nitroso-2-naphtols (1.14), prepared from (1.12) via (1.13) (Fig. 7).

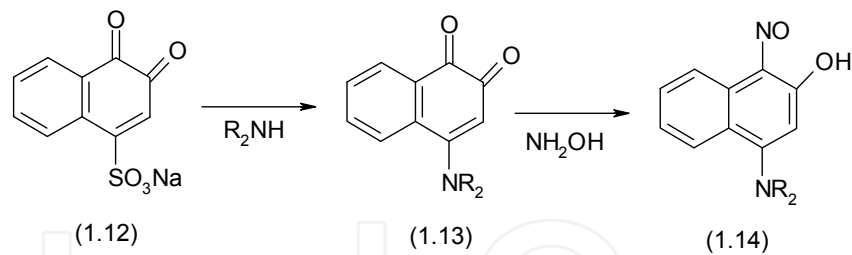


Fig. 7. Analysis of position 5 and 6' in synthetic route to spiroindolinonaphthoxazine

3.5.2 Spectral properties of spiroindolinonaphthoxazines

The λ_{\max} of the ring opened spiroindolinonaphthoxazine is at 590 nm. Also, they show a negative solvatochromic shift. Absorption moves hypsochromically (20-60 nm) in less polar solvents (Kim, 2007), Figure 8.

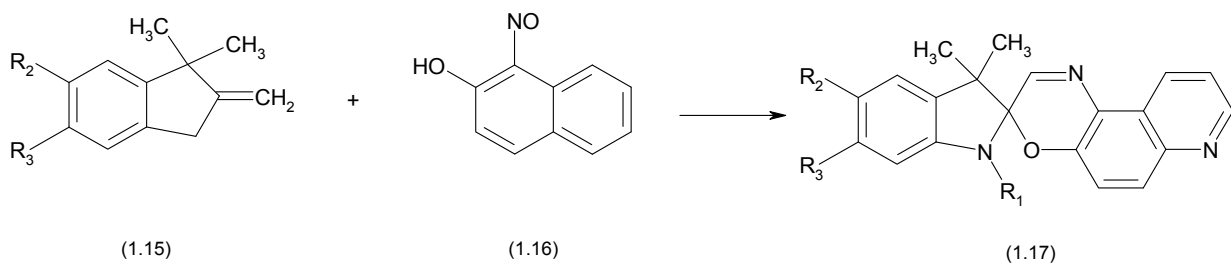


Fig. 8. Synthetic pathway to spiroindolinopyridobenzoxazines

Commercially important group of spiroxazines are those in which the naphthalene ring is replaced by quinoline to give spiroindolinopyridinobenzoxazines (1.17) (Suh et al. 2007). Synthesis is a reaction between 5-nitroso-6 hydroxyquinoline (1.16) with alkyl substituted 2-methylenindolines (1.15). The data on absorption effects caused by substitution on 5- and 6'-position are given in table 3.

6' - substituent	5 - substituent	λ_{\max} [nm]
H	H	605
Indolino	H	592
Indolino	OCH ₃	623
Indolino	Peperidino	637
Piperidino	H	578
Piperidino	Cl	568
Piperidino	CF ₃	560
Morphilino	H	580
Diethylamino	H	574

Table 3. Substituent effects on the absorption maximum of the coloured state of spiroindolinonaphthoxazines

3.6 Benzo and naphotpyrans (chromenes)

Both benzo and naphotpyrans are based on 2H-chromene ring system (Figure 9). These systems can be divided: 2H-benzopyrans (1.18) and three isomers of naphotpyrans (1.19-1.21). Due to the little or no photochromic behavior, isomer in 1.21 will not be discussed. Although substituents on R1 and R2 position may be a part of carbocyclic spiro ring, they are usually unconnected substituents such as gem dialkyl or aryl groups (Pardo, 2010).

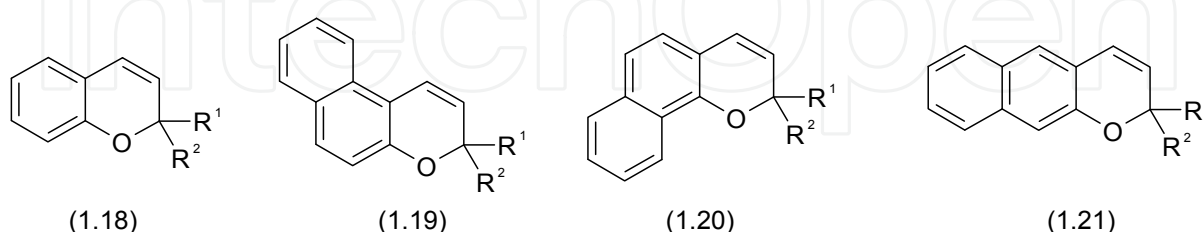


Fig. 9. Chemical structure of 2H-benzopyrans and three isomers of naphotpyrans

In terms of photochromic mechanism, it is quite similar to that of spiropyrans shown in Figure 10. Presence of UV irradiation induces cleavage of C-O ring, thus breaking the pyran ring and giving zwitterionic form or more likely cis- and trans-quinoidal forms (1.16). Studies on the dynamics of the reaction have shown that formation of cis-quinoidal form occurs in picoseconds, followed by trans-form in nanosecond. Isomers (1.19) and (1.20) show quite different photochromic behavior. Isomer (1.20; R1,R2=Ph) produces a more bathochromic coloured activated state than (1.19; R1, R2=Ph) ($\lambda_{\max} = 481 \text{ nm}$ vs 432 nm), a large increment in colouration, but a very slow fade rate back to the inactivated state.

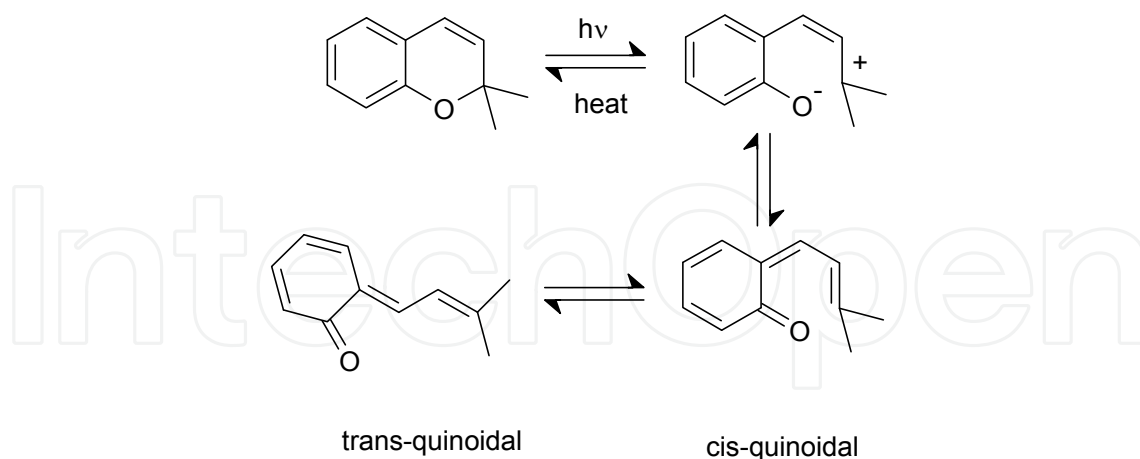


Fig. 10. Photochromic behavior of chromenes

3.6.1 Synthesis of benzopyrans and naphotpyrans

The synthetic method for more important 2,2-diaryl derivatives (1.25) involves the reaction of 1,1-diarylprop-2-yn-1-ol (1.24) with a substituted phenol or naphthol in the presence of acid catalyst. The alkynols are prepared by reaction of benzophenone (1.22) with Na or Li derivative of an alkynide, such as the trimethylsilyl acetylide (1.23), Figure 11.

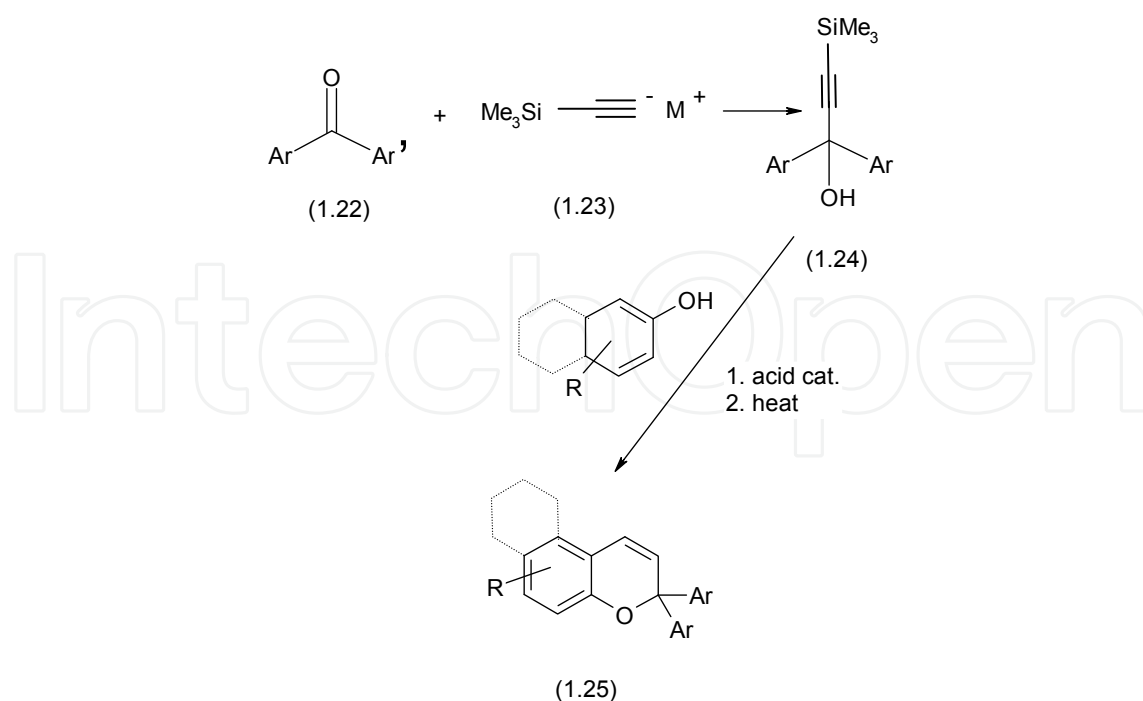


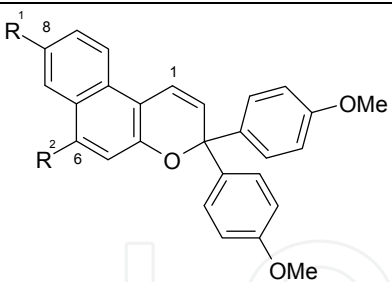
Fig. 11. Synthesis of diaryl benzo- and naphthopyrans

3.6.2 spectral and physical properties of diarylnaphthopyrans

Like the classes of spirobenzopyrans and spironaphthoxazines, diarylnaphthopyrans show significant solvatochromic behaviour. Influence of the substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphtho[2,1-pyrans] (tab. 4 and 5).

R ¹	R ²	λ_{\max}	ΔOD	T _{1/2} [s]	Solvent
H	H	430	-	11	A
H	4-MeO	458	-	8	A
H	4-CF ₃	422	-	28	A
4-MeO	4-MeO	475	-	3	A
4-MeO	4-CF ₃	440	-	4	A
4-MeO	4-NMe ₂	512	-	1	A
4-NMe ₂	4-NMe ₂	544	-	0,5	A
H	H		0,36	45	B
2-F	4-MeO	456	1,0	170	B
2-F	3,4-diMeO	472	1,05	203	B
2-Me	4-MeO	469	2,40	600	B
2,6-diF2	4-MeO	450	2,23	1800	B

Table 4. Influence of substituents in the 3-phenyl rings on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans (A = toluene solution; B = imbeded into diethyleneglycol bis(allyl carbonate) polymer)



R ¹	R ²	λ_{\max}	IOD	IODF ₁₀ %	Solvent
H	H	475	0,20	50	A
MeO	H	456	1,89	7	A
H	MeO	502	0,55	41	A
H	H	475	0,12	45	B
MeO	H	456	1,42	10	B
Piperidino	H	452	1,95	11	B
Piperidino	H	452	1,95	13	B

Table 5. Influence of substituents in 6- and 8-positions on the properties of 3,3-diaryl-3H-naphtho[2,1-b]pyrans (A = polyurethane; B = Spectralite)

Whereas:

IODF₁₀ - percentage loss in initial optical density 10s after removing UV irradiation source

λ_{\max} - refers to the absorption maximum of the coloured state

ΔOD - the change in optical density (absorbance) on exposure to the xenon light source

$t_{1/2}$ - fade rate, time expressed in seconds for the ΔOD to return to half of its equilibrium value.

4. Textile applications

Photochromic compounds as the ones represented in this chapter are commercially available from a number of suppliers, such as: Sigma Aldrich, PPG Industries and James Robinson. So far, virtually all application techniques have been investigated in efforts of functionalizing the textile fiber with photochromic systems. Some application methods have been proven advantageous over the other, such as embedding into the polymer matrix in the spinning phase of the "man-made" fibers (polypropylene). Other processes may include dyeing and screen printing, which are considered more appropriate since the demand on photochromic textiles is limited to piece garments, rather than to batch production (Billah, 2008; Canal, 2008; Nelson, 2002).

4.1 Exhaust dyeing with photochromic compounds

The group of authors of this chapter has made significant efforts in functionalizing textile fibres with photochromic dyes. Therefore, this chapter will give a review of several papers covering this issue, namely application of photochromic compounds using the means of exhaust dyeing. In the context of dyeing technology, photochromic compounds may be observed as disperse dyes appropriate for dyeing "man-made" fibres. The dyeing process has to be set accordingly.

Most of the investigation were done using Sigma Aldrich dyes of 97% purity and alterations on the level of the dye molecule were made. Selected dyes are shown in the Table 6.

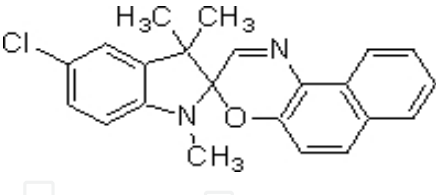
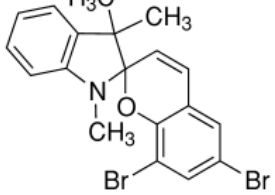
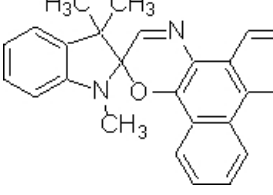
 <p>5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4)oxazine]</p> <p>D1</p>	 <p>1',3'-Dihydro-8-methoxy-1,3,3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]</p> <p>D2</p>	 <p>1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4)oxazine]</p> <p>D3</p>
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Table 6. Selected photochromic dyes

Photochromic dyes were prepared by dissolving in small quantities of acetone AC, as dissolving in acetone results in clear solutions, exhibiting photochromic reaction under UV-A ($\lambda_{\max} = 354\text{nm}$). Fibres chosen for the investigations were PA6 and PES, while the process of dyeing was set to satisfy the demands of disperse dyes. Exhaustion of dyes from the dyebath and onto the fibre was done according to the schematic of the process in the Figure 12. Textile substrates were dyed under laboratory conditions in Polycolor Mathis dyeing apparatus. Dyeing was commenced at 25 °C and was raised gradually to 100 °C and continued at that temperature for another 60 minutes. Textile samples were then rinsed at 40 °C, followed by hot rinsing at 80 °C.

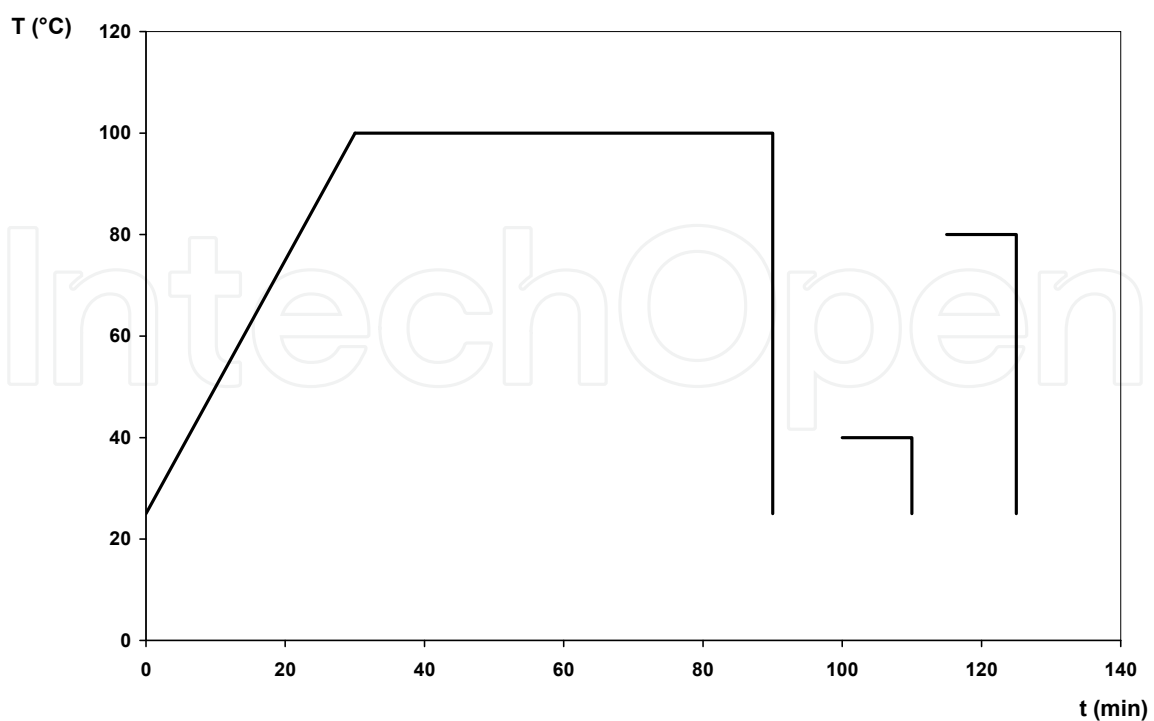


Fig. 12. Schematic of the dyeing process

Textile samples were dyed in concentrations of 0,1%, 0,3%, 0,5% and 1% calculated according to weight of fibres. Liquor to goods ratio was set to 1:20 and pH set to 4,5. Materials were dyed according to the process scheme shown in Figure 11. Kemonecer WET (non-ionic tenside) was used as an auxiliary chemical acting as a surfactant.

To investigate photochromic property of obtained photochromic textiles, samples were submitted to source of UV light in Solarscreen Test Camber to determine photochromic effect. Samples were irradiated in periods of 10, 20, 40 seconds and spectrophotometrically measured accordingly to determine the ability to respond to UV light. Fade was done by exhibiting in dark in the very same intervals in which the samples were irradiated. Spectrophotometric measurement was done on Datacolor, Spectraflash SF-600 CT-PLUS®. Photochromic property was expressed through K/S values (eq. 3) (Fig. 13 and 14) and a^*/b^* coordinates (Fig. 14) calculated from value of remission.

$$K/S = (1 - R^2) / 2R \quad (3)$$

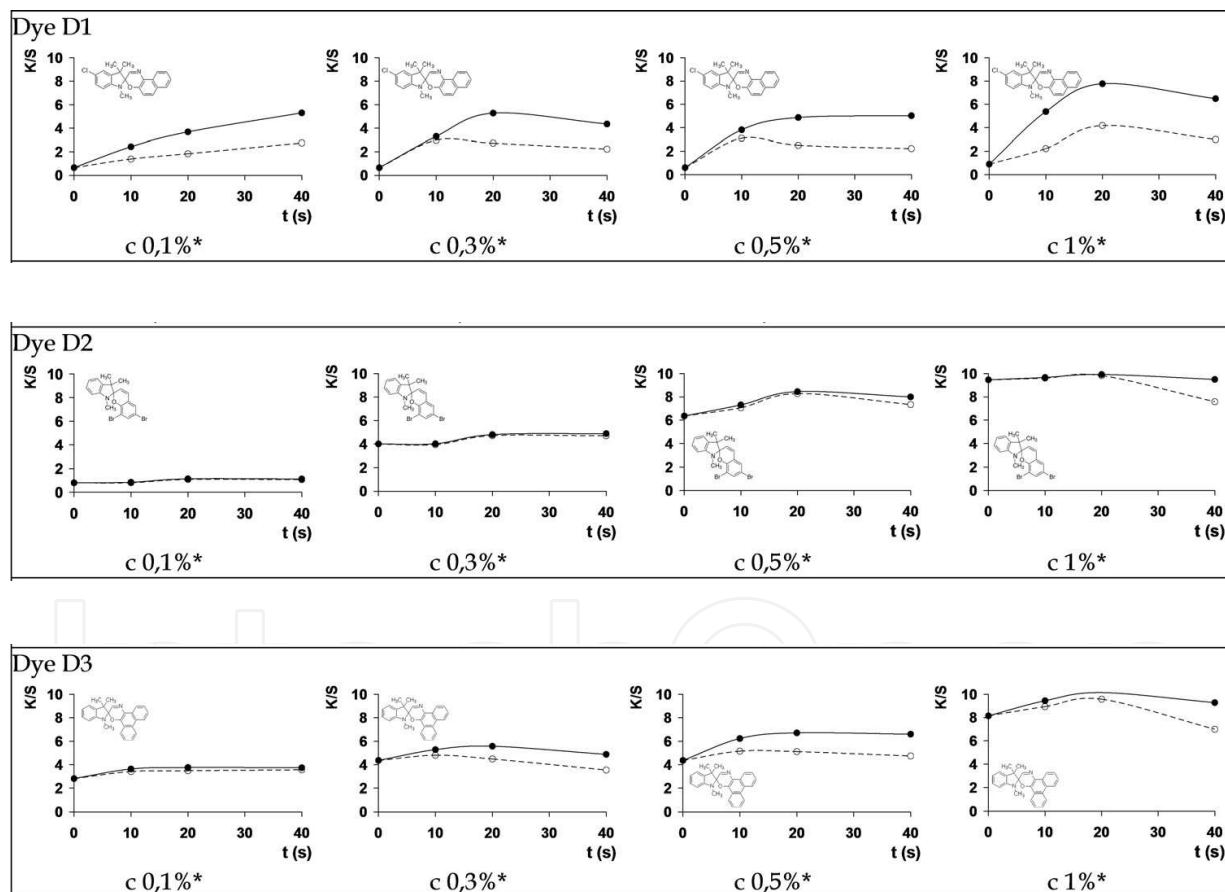


Fig. 13. K/S value of PA fibre vs. concentration of the dye (* on weight of the fibre (owof)) (— UV irradiated samples, --- after removal from UV source)

As seen in K/S graphs, PA is considered more suitable substrate for applications of photochromic dyes, while low obtained K/S values of PES substrate indicate this fibre unsuitable for dyeing by photochromics. Significant influence of dye concentration on

obtained K/S values was obtained with maximum value ($K/S \approx 8$) reached after 20 seconds UV irradiation time for PA sample dyed by 1% of Dye 1. Dyeing by Dye 3 resulted in colored substrates (PA and PES) of distinct photochromic property expressed through increased K/S values measured at same wavelength ($\lambda_{\max PA} = 600 \text{ nm}$).

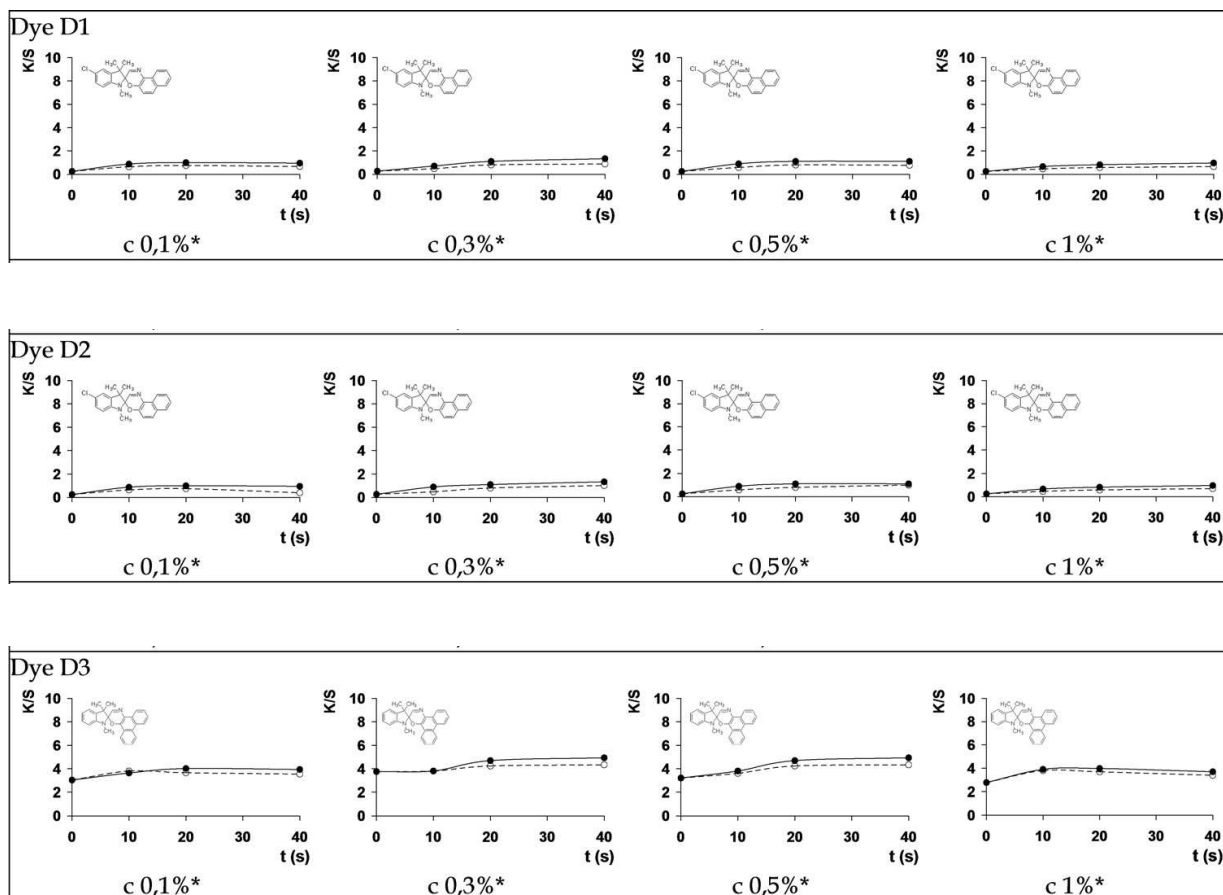


Fig. 14. K/S value of PES fibre vs. concentration of the dye (* on weight of the fibre (owof)) (— UV irradiated samples, --- after removal from UV source)

Low K/S value obtained for PES fibres confirm the influence of fibres structure on effectiveness of the dyeing process which was found to be appropriate for PA fibres, while in the case of PES carrier should have been added or process carried out at higher temperature than $100 \text{ }^\circ\text{C}$. Ideally, this would increase the volume of amorphous area in PES by decreasing crystallinity. Because of low obtained values for PES fibres only a^*/b^* coordinates for PA fibres are shown (Fig. 15).

Shown a^*/b^* graphs refer only to PA samples dyed by the greatest investigated amount of dye (1% owof) (Fig. 15).

Lowest color depth was obtained in PA samples dyed by D1. After exposition to UV, lightness of the samples (D1-PA) increases, while chromacity is less than in samples dyed by D2 and D3, although difference in chromacity of UV irradiated and unirradiated sample is greatest in PA samples dyed by D1. Aforesaid, suggests the advantage of subjective reasoning over reading instrumental data only.

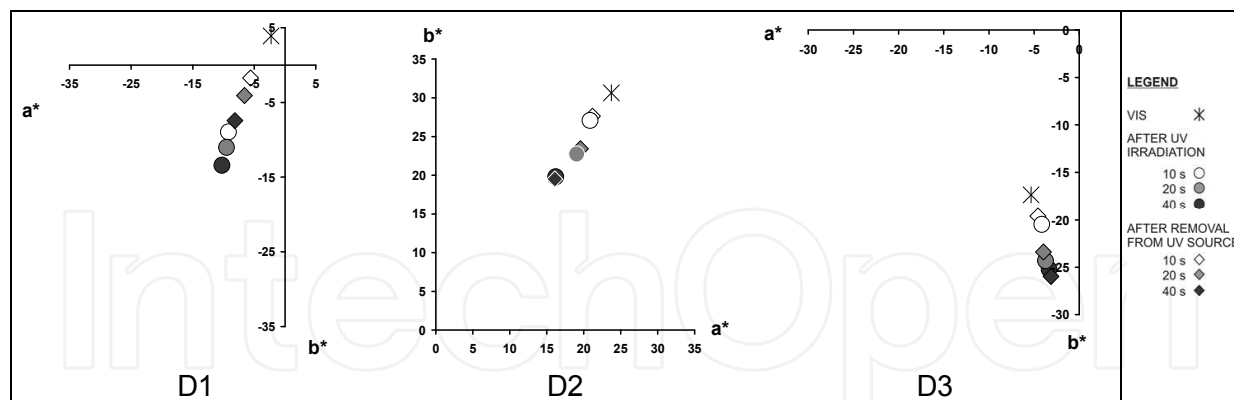


Fig. 15. a^*/b^* coordinates of PA samples dyed by 1% (owof) of photochromic dye

5. Conclusion

During the last ten years the traditional textile industry, that during the decades has favored quality, has changed its strategy to support the innovation and the creation of new products and functionalities. Accordingly, a rapidly growing trend is noticeable in the field of smart fabrics and intelligent textiles that can sense and react to environmental conditions or stimuli from mechanical, thermal, chemical, electrical or magnetic sources. Research by this group of authors supports and represents a contribution to the field of testing and optimization applications of photochromic dyes in textiles. In the future, research of the authors will be aimed at analyzing photochromic textile materials using state of the art instrumental analyses, such as FTIR and HPLC, supported by different spectrophotometric methods. Potentials of these materials will be researched in terms of sensory properties, with emphasis on their accuracy to react in preprogrammed manner to a very specific level of ultraviolet irradiation. Relationship among colour strength and UV irradiation levels will be researched using statistically designed experiments. In terms of application methods, screen printing will be given most attention, this statement being supported by the fact that presence of photochromic dyes or pigments is needed only on the surface of the textile material. This would well broaden the number of substrates, whereas in dyeing, only a small number is really suitable. In regards to the price of the final product, printed substrates should be favoured due to their obvious economical viability and feasibility. In terms of ecology, exemption of wastewater should be advantageous over dyeing.

In terms of "high added value" photochromic textiles should be considered as such, while the number of functions is increased significantly when compared to conventional textiles. Colour phenomenon is used to sense and detect harmful UV rays, while it is only exhibited under irradiation of UV light. Therefore, one can speak of colour at the right time, rather than of colour all the time. Dyes described in this paper may also provide necessary protection from UV spectra, while the energy is used for rearrangements on molecular level of the dye, thus increasing the number of conjugated double bonds, which is experienced as colour.

From this paper one could conclude great potentials of such dyes as described in this paper. Research and results shown imply to broadened use of photochromic dyes and expansion possibilities from ophthalmics to virtually any polymer if applied properly.

6. Acknowledgment

The research funded by Croatian Ministry of Science, Education and Sports, within an approved scientific project: Colours and Dyes in Processes of Ecologically Acceptable Sustainable Development.

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Textile Dyeing

Edited by Prof. Peter Hauser

ISBN 978-953-307-565-5

Hard cover, 392 pages

Publisher InTech

Published online 14, December, 2011

Published in print edition December, 2011

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