International Journal of Occupational Safety and Ergonomics (*JOSE*) 2009, Vol. 15, No. 3, 243–254

Application of a Photochromic Dye in an Automatic Welding Filter

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The main purposes of this study were to select a photochromic dye and to develop an active welding filter with a photochromic layer. A series of functionalized spirobenzopyranoindolins were synthesized and their photophysical and photochemical properties were investigated in a solution using absorption and emission spectroscopy. Time-resolved fluorescence spectroscopy measurements were used to characterize the decays and rate constants of fluorescence emission. One dye was selected as a suitable photoactive compound in automatic welding filters. A model of an active welding filter with a photochromic layer based on 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indole] (6-nitroBIPS) was developed. The paper presents the results of tests of the filter conducted according to EN standards.

automatic welding filter welding photochromic dyes spirobenzopyranoindole

1. INTRODUCTION

Workers' exposure to intensive ultraviolet (UV), visible and infrared (IR) radiation during welding is dangerous. Radiation generated during electric welding can cause serious effects, e.g., cataracts (because the eye is overheated), inflammation of the cornea and conjuctiva, and changes in the welder's retina and fundus of the eye. Additionally, melted metal spatter and cinder can seriously injure the eyeball.

During welding, glasses, goggles and face shields with optical filters protect against radiation. Because visible radiation emitted by welding arcs is very intensive, it is necessary to use very dark filters, with a light transmittance coefficient from 0.1600% (protection level 8) to 0.0012% (protection level 12). Such dark filters make it impossible to see the welded object before the welding arc is struck. That is why the worker is forced to glance at the welding process when the welding arc is struck. This momentary glance can result in cataracts, welders' occupational disease [1].

Automatic welding filters with a variable shade number are an effective solution to this problem. These filters change the luminous transmittance coefficient from 1.20% (shade number 4) in the light state to 0.16% (shade number 10) in the dark state, in under 0.5 ms [2, 3].

Currently available filters consist of a liquid crystal screen, solar panels, an electronic module and detectors reacting to the striking of the welding arc. Because of their complex design, these filters are expensive and thus available to few welders. Hence, research aimed at developing an active welding filter using photochromic reactions of spirobenzopyranoindolins.

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic

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radiation between two forms with different absorption spectra. The most prevalent organic photochromic systems involve unimolecular reactions. Usually, photochromic molecules have a colorless or pale yellow ground state form and a colored excited form (e.g., red or blue). Photochromism and the subsequent thermal relaxation processes of numerous organic dyes have been investigated, e.g., for spiropyranoindolins, spirooxazines, chromenes, fulgides and fulgimides and diarylethenes [4].

Among photochromic dyes, spirobenzopyranoindiolins are a major class of organic photochromes with a high quantum yield and a reversible photochromic reaction. Researchers have synthesized and investigated a long series of spirobenzopyranoindolins. The first chemical characteristic of spirobenzopyranoindolins, discovered at the beginning of the 20th century, was the reversible transformation into colored forms. It takes place during dissolution in solvents, during heating or under the influence of UV radiation [5]. Especially numerous experiments involved 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyrano-2,2'-indole] (6-nitroBIPS); they included low temperature absorption [6], triplet sensitization, femtosecond [7] and nanosecond [8] time-resolved UV-VIS pump probe spectroscopy, time-resolved resonance Raman spectroscopy [9] and attenuated total reflection spectroscopy [10]. The general scheme for such transformations consisted of initial formation, during cleavage of the Cspiro–O bond, of a [2H]chromene fragment of a bipolar form, which could be transformed into a merocyanine form with a different configuration for the polymethine chain. Growing interest in a new generation of storage devices, sensors, active optical devices and optical filters prompted the development of new functional photochromic compounds [5]. Theoretical investigations of the effect of substituents on the spectral characteristics of photoinduced forms made it possible to find a range of compounds with a strong bathochromic shift of the long-wave band in the open-chain isomer. This is primarily achieved by the introduction of π-accepting substituents, such as the nitro group, into the benzene ring of the chromene part of spiropyrans [5].

We studied the photophysics and photochemistry of a series of spirobenzopyranoindolins in solvents of different polarity (Figure 1) using steady-state and time-resolved spectroscopy. The main purpose of this study was to use selected spirobenzopyranoindoles dissolved in an organic solvent to construct an active welding filter which changes its transmittance during the welding process.

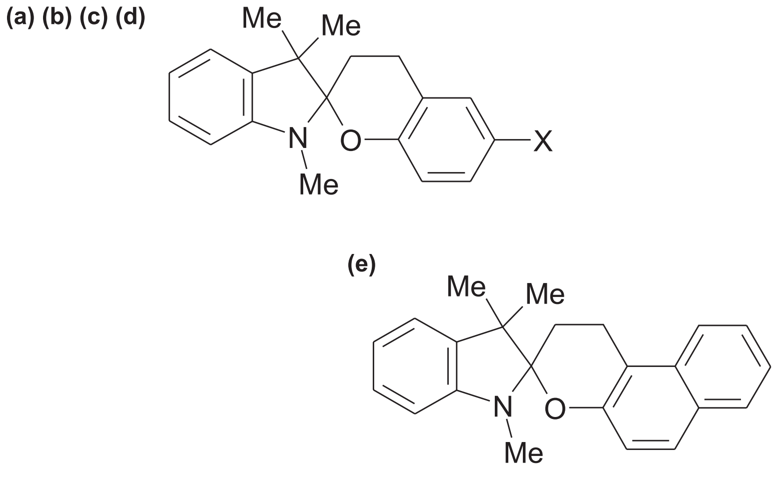

Figure 1. Synthesized series of spirobenzopyranoindolins: (a) 1',3',3'-trimethylo-6-bromo[2H-1-benzopyrano-2,2'-indolin]; (b) 1',3',3'-trimethylo-6-nitrospiro[2H-1-benzopyrano-2,2'-indolin]; (c) 1',3',3'-trimethylo[2H-1-benzopyrano-2,2'-indolin]; (d) 1',3',3'-trimetylo-6-sulfospiro[2H-1-benzopyrano-2,2'-indolin]; (e) 1',3',3'-trimetylo-spiro[3H-Benzo[f]chromeno-2,2'-indolin]. *Notes.* X—Br, NO_2, H, SO_3H.

2. MATERIALS

Spirobenzopyranoindolins were synthesized according to the literature [5, 8, 11, 12] and purified with crystallization using ethanol. Their structures were confirmed with 1H NMR spectroscopy. The solvents were HPLC grade and were used as supplied, without further purification. All solvents were purchased from Sigma Aldrich (USA).

3. EXPERIMENTAL METHODS

Absorption spectra were obtained using a Cary 5E spectrophotometer (Varian, Australia). Fluorescence measurements were conducted with a Fluorolog 3 fluorimeter (HORIBA Jobin Yvon, USA). Merocyanine formation was inducted using a high pressure HBO 250 W UV lamp (Osram, Germany). The decays of florescence were collected with a spectrophotometer (Edinburgh Analytical Instruments, UK). An nF900 nanosecond hydrogen lamp (Edinburgh Instruments, UK) with a repetition rate of 40 kHz was used as a pulsed excitation source. Three synchronously working photomultiplier devices were used as detectors. The resolution of the setup was experimentally estimated to be 50 ps.

Switching time of an active welding filter was measured using a PCSU 1000 digital storage oscilloscope (Velleman, USA); an ELWA 18LA2 flash lamp (Poland) was a source of irradiation.

4. RESULTS AND DISCUSSION

4.1. Steady-State of Absorption and Fluorescence Measurements

The spirobenzopyranoindolins (Figure 1), synthesized according to the method described in section 3, were irradiated using a UV lamp with a broad emission spectrum with a maximum of ~350 nm. During irradiation, the absorption spectra of merocyanine forms were collected. Table 1 shows the results of steady-state absorption and fluorescence spectroscopy measurement of a synthesized series of spirobenzopyranoindolins.

An analysis of data on the spectrum distribution of welding arcs showed that the most intensive emission of UV radiation took place for the 340–380 nm range. That is why the photochromic compounds in the ground state have to absorb UV radiation from that range, and the merocyanine form of photochromic dyes should show maximum absorption in the 550–600 nm range (i.e., the maximum sensitivity of human eyes).

Among synthesized spirobenzopyranoindolins, the properties of photo-excited 1’,3’,3’-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2’-indole] were of special interest to us, since it showed absorption of 605 nm in the excited state (Figure 2) and a high quantum yield of photochromic reactions [13, 14]. A nitro group at the 6-position of the benzopyran moiety could be expected to strongly enhance intersystem crossing, thereby changing the reaction pathway in photocoloration and shift the equilibrium towards the open form [8].

TABLE 1. Steady-State Absorption and Fluorescence Data of Spirobenzopyranoindoles in Cyclohexane

	Absorption (nm)		Fluorescence Measurement (nm)	
Compound	λ_{maxSp}	λ_{maxMc}	λ_{exc}	λ_{emis}
a	295	425	280, 300	352, 672
b	262, 325	605	369, 540	643, 681
c	288	415	278	354, 677
d	239, 276	—	320, 390	442, 571
e	245, 299	425	277	355, 558

Notes. a, b, c, d, e—see Figure 1; λ_{maxSp}—absorption maximum of absorption spectra of spiropyran form, λ_{maxMc}—absorption maximum of absorption spectra of merocyanine form, λ_{exc}—maximum of excitation spectra, λ_{emis}—maximum of emission spectra.

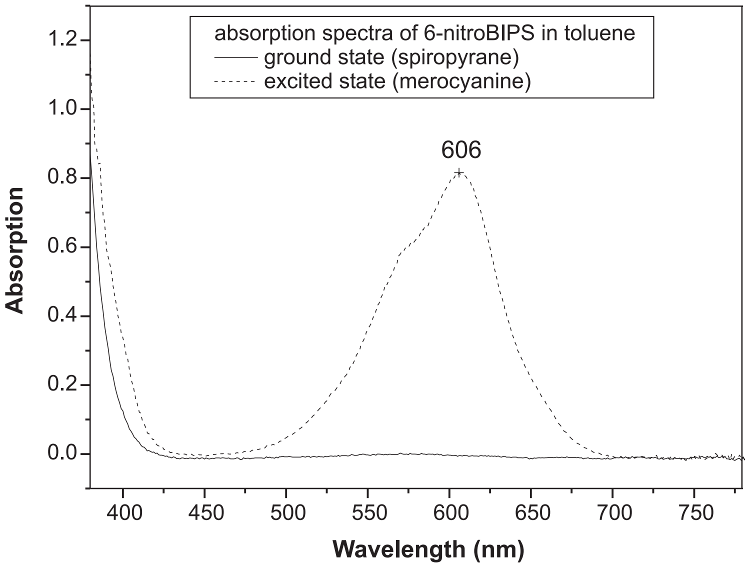

Figure 2. Absorption spectra of 6-nitroBIPS in ground and excited states in toluene.

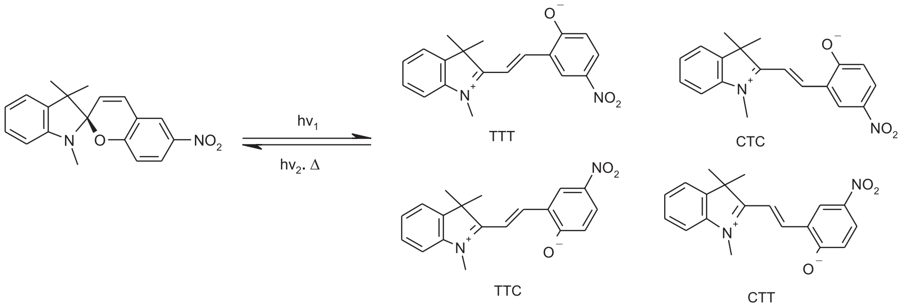

Figure 3. Diagram of tautomerization and isomerization of 6-nitroBIPS upon ultraviolet excitation.

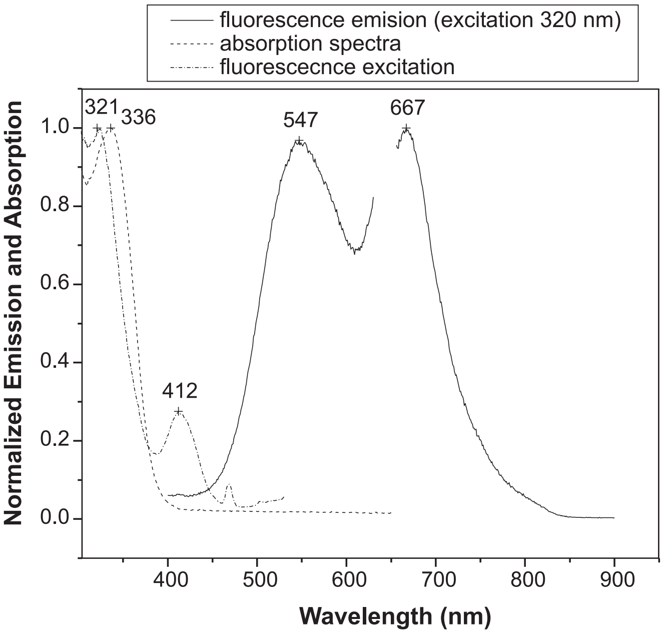

Figure 4. Normalized absorption, fluorescence emission and excitation spectra of 6-nitroBIPS in toluene.

Upon UV excitation, the ring opens and cis-trans isomerization follows [6, 8, 15, 16]. The appearance of a new absorption band results from the charge shift under excitation of the molecule. This band is usually called a charge transfer band (CT). Figure 3 illustrates tautomerization and isomerization of 6-nitroBIPS [17] upon UV excitation.

The presence of at least two isomers is suggested by the fluorescence emission and excitation spectra (Figure 4). Depending on the wavelength at which fluorescence emission is measured (550 or 670 nm), the maximum of the excitation spectrum shifts from 321 to 412 nm. Thus, these data could be interpreted by assuming the presence of at least two isomers in a toluene solution. The fluorescence emission at 547 nm possibly corresponds to one of the isomers and fluorescence emission at 667 nm corresponds to the other one. It is not possible to dimerize in photochromic systems [4, 5]. There is no information on this phenomenon in the literature. Wohl and Kuciauskas also obtained this model in their time-resolved fluorescence studies [17].

4.2. Solvent Polarity Influence on Absorbance of 6-nitroBIPS in Excited State

The results also show a significant influence of solvent polarity on absorption spectra of the excited state of the 6-nitroBIPS. Figure 5 shows the shift existing in absorption of the excited state due to the rather big difference in the polarity of the solvent.

In the excited state of 6-nitroBIPS a shift of absorption maximum towards the blue range of the visible region was observed. In a nonpolar solvent (e.g., toluene) the maximum of absorption is observed at 608 nm and in a polar solvent (e.g., acetonitrile) at 557 nm.

We did not observe any shift of absorption spectra of 6-nitroBIPS for all selected solvents dependently on concentration of the 6-nitroBIPS.

4.3. Time Dependent Fluorescence Studies

Time correlated single photon counting (TCSPC) involves counting electric impulses attributed to emitted photons as a function of time. The repetition rate of the excitation source was controlled by a pulse generator. Light emitted by an excited sample passed through an emission monochromator and then photons were collected by a photomultiplayer. The slits in the excitation and emission part were 10 and 1 mm, respectively. The experimental time window was divided into 1 023 channels, each 0.09 ns wide. The reference sample used in studies with this setup was a colloidal suspension of Ludox silica (Grace, USA). As a result of data collection a curve describing the decay of fluorescence as a function of time was obtained. The decays were

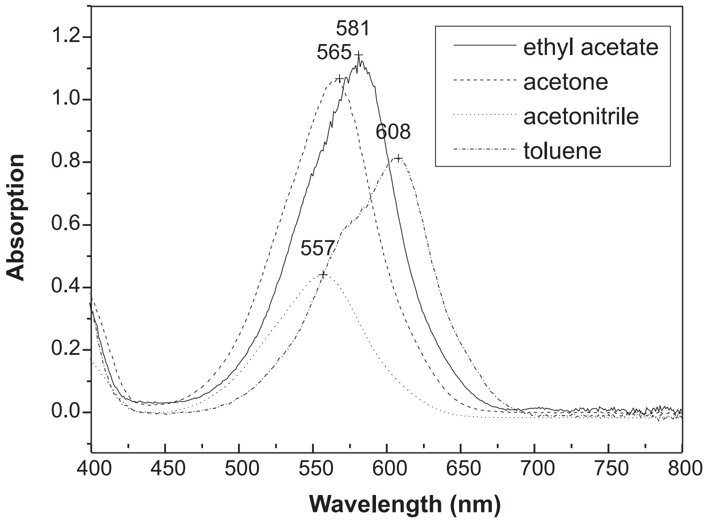

Figure 5. Absorption spectra of the excited state (merocyanine) of 6-nitroBIPS of 10^{-3} mol/dm^3 in selected solvents.

successfully fitted to the function described with Equation 1 [18]:

$$I(t) = \sum B_i \, e^{-(t/\tau_i)}, \qquad (1)$$

where $I(t)$—intensity of fluorescence, B_i—pre-exponential factor, τ_i—lifetime of i component.

The lamp pulse decay was subtracted from the collected data with the Edinburgh Analytical Instruments program [19].

The lifetime values of synthesized spirobenzopyranoindolins in acetonitrile, calculated with the least squares method from TCSPC measurements, are presented in Table 2. The longest lifetime values were obtained for compound 1d (1',3',3'-trimethylo-6-nitrospiro[2H-1-benzopyrano-2,2'-indolin]) and the shortest for 1e (1',3',3'-trimetylo-spiro[3H-Benzo[f]chromeno-2,2'-indolin]). Figure 6 illustrates an example of the decay of fluorescence of 1',3',3'-trimethyl-6-bromo[2H-1-benzopyran-2,2'-indolin] in acetonitrile collected with TCSPC. The lifetime values of 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indole] for all studied solvents calculated with the least squares method from TCSPC measurements are presented in Table 3.

The obtained values of lifetimes for compound 1b (1',3',3'-trimethylo-6-nitrospiro [2H-1-benzopyrano-2,2'-indolin]) correspond to those of Wohl and Kuciauskas [17]:

TABLE 2. Lifetime Values, τ, of Spirobenzopyranoindoles in Acetonitrile Calculated With the Least Squares Method From Time Correlated Single Photon Counting Measurements

	Compound				
Parameter	**a**	**b**	**c**	**d**	**e**
τ (ns)	1.93 ± 0.01	0.20 ± 0.02	6.08 ± 0.02	6.40 ± 0.02	8.57 ± 0.14 0.53 ± 0.02
χ^2	1.125	0.870	0.999	1.045	1.117

Notes. a, b, c, d, e—see Figure 1; χ^2—fitting quality.

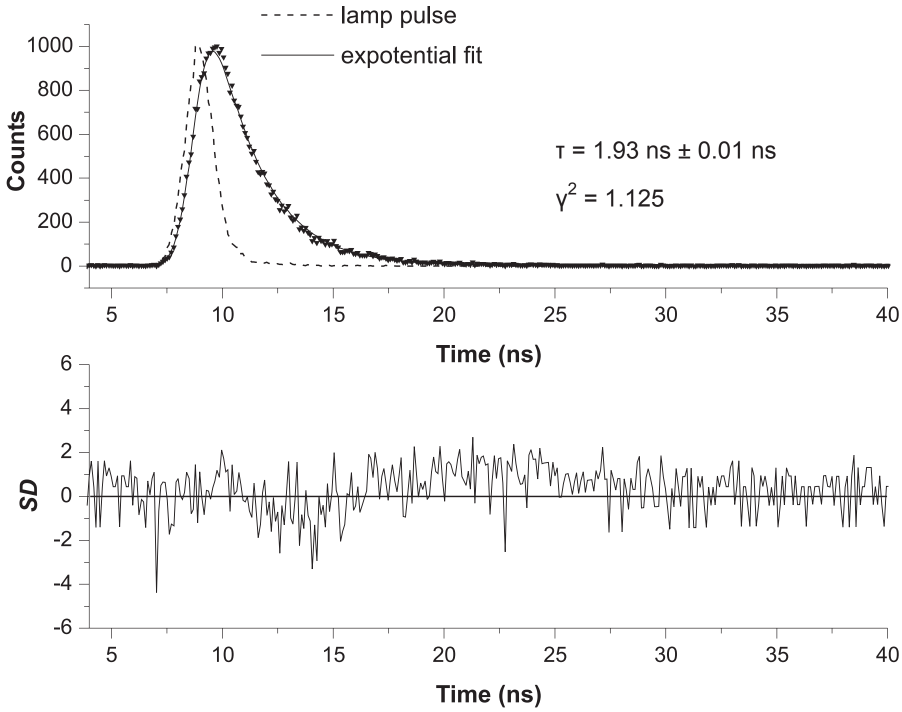

Figure 6. Decay of fluorescence of 1',3',3'-trimethyl-6-bromo[2H-1-benzopyran-2,2'-indole] in acetonitrile together with the exponential fitting function (black line) and a response of the excitation source (dotted line).

- excitation at λ_{exc} = 630 nm results in faster bleach recovery than excitation at λ_{exc} = 490 nm:
- the ground-state recovery measured with λ_{exc} = 630 nm was described by a 67 ± 5 ps lifetime single-exponential decay;
- the λ_{exc} = 490 nm ground-state recovery yielded more complex kinetics that required a biexponential fit with $\tau_1 = 36 \pm 4$ ps and $\tau_2 = 270 \pm 25$ ps.

TABLE 3. Lifetime Values, τ, of 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indole] for Some Solvents Calculated With the Least Squares Method From Time-Correlated Single Photon Counting Measurements (λ_{exc} = 490 nm)

	Solvent		
Parameter	**acetonitrile**	**chloroform**	**cyclohexane**
τ (ns)	0.20 ± 0.02	0.25 ± 0.01	0.16 ± 0.02
χ^2	0.870	1.060	0.903

Notes. χ^2—fitting quality.

Görner also reported that the major deactivation process of the excited trans isomers was trans-cis photoisomerization and fluorescence [15]. A nitro group at the 6-position of the benzopyran moiety is expected to strongly enhance intersystem crossing, thereby changing the reaction pathway in photocoloration. Also the fluorescence lifetimes were longer when polar solvents were used (Table 4).

TABLE 4. Fixed Relaxation Rate Constants of 6-nitroBIPS in Selected Organic Solvents

Solvent	Dipole Moment of the Solvent (D)	Fixed Rate Constants of the Dye (s^{-1})
Dimethyloformamide	3.80	(2.2 ± 0.1) 10^{-3}
Ethyl acetate	1.78	(3.1 ± 0.1) 10^{-2}
Toluene	0.36	(7.1 ± 0.4) 10^{-2}
Chloroform	1.01	(2.5 ± 0.1) 10^{-2}
2-Ethoxyethanol	0.31	(4.3 ± 0.5) 10^{-4}
Hexane	0.05	(5.1 ± 0.1) 10^{-2}
Decane	0.06	(6.0 ± 0.4) 10^{-2}
Xylene	0.34	(7.2 ± 0.1) 10^{-2}

4.4. Kinetics of Relaxation Reaction

Figure 7 shows examples of absorption curves of the decay of the excited state of 6-nitroBIPS in different solvents.

The decays were successfully fitted to the function described with Equation 2:

$$[A] = [A_0] \cdot e^{-k \cdot t}, \qquad (2)$$

where A—concentration of the dye at t time; A_0—original concentration of the dye; k—rate constant. Table 4 shows fixed relaxation reaction

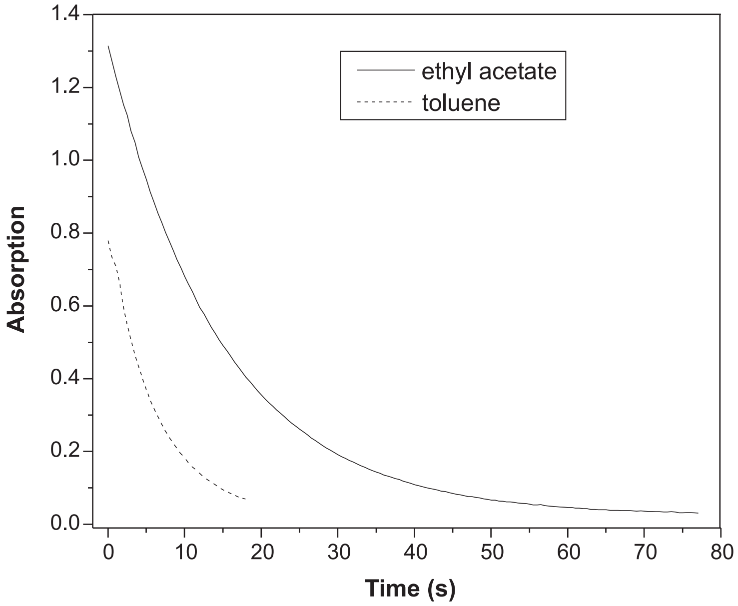

Figure 7. Examples of absorption spectra of the decay of the excited state of 6-nitroBIPS in different solvents.

constants of 6-nitroBIPS in a solvent with different polarity calculated with Equation 2.

Testing relaxation kinetics of 6-nitroBIPS in organic solvents showed that the reaction speed increased as the solvent polarity decreased. The best results were obtained when the reaction occurred in toluene (fixed reaction speed of 0.0706 s^{-1}). However, because 6-nitroBIPS has a relatively low resistance to UV radiation in toluene and also low solubility in this solvent (which significantly limits obtaining photochromic filters of appropriate density), a solution of ethyl acetate was used in constructing active welding filters.

5. CONSTRUCTION OF PHOTOCHROMIC WELDING FILTERS

An analysis of data on the spectrum distribution of welding arcs has shown that most intensive emission of UV radiation takes place at the wavelength of 330–360 nm. So it was assumed that an active photochromic dye should absorb of UV radiation in this range. Because human eyes are most sensitive at ~550 nm, it was assumed that the excited state of the dye should have maximum absorption in the 560–600 nm range.

Photochromic dyes in the excited state absorb visible radiation in a narrow range (~60 nm) [4], so it was necessary to use interference filters which cut off visible radiation not absorbed by the dyes. Interference filters must cut off visible radiation in the 380–560 and 600–780 nm ranges. Transmittance in this range should not exceed 0.001%, so for the 520–580 nm range this value should reach at least 20%. Because welding arc radiation is also associated with intensive IR radiation, a passive IR absorption filter had to be used, too.

The developed model of an active welding filter based on a photochromic system consists of (a) a photochromic layer (a photochromic dye diluted in an organic solvent) activated by welding arc radiation; (b) a glass absorption filter absorbing IR radiation; (c) interference filters blocking UV and IR radiation; (d) interference band-pass filters transmitting visible radiation of 560–600 nm. Figure 8 is a diagram of an active welding filter.

5.1. Photochromic Filter Activated With Welding Arc Radiation

Research showed it was best to use 6-nitroBIPS dissolved in ethyl acetate. 6-nitroBIPS in this solvent had the absorption maximum at 605 nm in the excited state, high solubility and a quantum yield of the photochromic reaction and the highest resistance to UV radiation. An active filter cuvette was made of glass panels glued to one another and filled with a concentrated solution of the dye in ethyl acetate.

5.2. IR Radiation Absorbing Filter

Commercially available Athermal SCHOTT (Germany) welding filters with protection level 3 and medium IR radiation transmittance coefficient of 0.75% were used in developing a model of an active welding filter.

5.3. Interference Filters

IR absorption filters were used as a basis of inference filters. Interference filters were made using vacuum evaporation and an electron

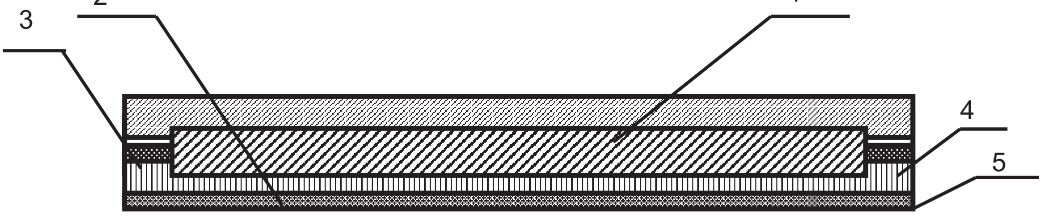

Figure 8. Sections of an active welding filter. *Notes.* 1—a quartz or sodium glass panel; 2—a liquid photochromic filter; 3—an infrared radiation absorbing filter; 4, 5—interference filters transmitting visible radiation of 560–600 nm.

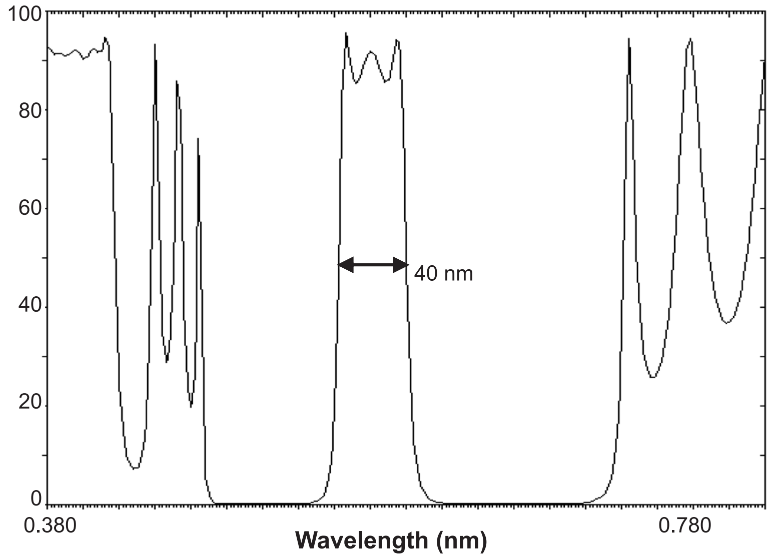

Figure 9. Transmittance spectrum of an interference filter with a bandwidth of 40 nm.

cannon. TiO_2 – H, a material with a high index of refraction, and SiO_2 – L, a material with a low index of refraction, were used to make the inference layers. Figure 9 illustrates the spectrum of the interference filter.

5.4. Test Results

The following protective parameters of the obtained filter were verified: (a) UV radiation resistance, (b) light transmittance coefficients in bright and dark states, (c) spectral transmittance in UV and average spectral coefficients of IR radiation transmittance, and (d) switching time of active welding filters. The value of the light transmittance coefficient of the filter in the light state was within the limits defined for protection level 5.

Because it was impossible to determine light transmittance coefficients in the dark state with a spectrophotometer, experiments were conducted in which this parameter was determined during exposure to welding arc radiation, when welding was done with a covered electrode. This welding technique was selected due to its popularity especially among small companies involved in welding and because of the highest stability of the radiation source, in relation to other welding methods. The tests were conducted on welding filters mounted in a welding shield fitted with an external protective cover plate made of polyester.

Due to the changing intensity of welding arc, 15 measurements were made for each position of the filter. The welding arc generated with a Nordika welding device (Telwin, Italy) was the source of radiation. An L-20a luxometer (Sonopan, Poland) was used for measuring the light transmittance coefficients. The filter and the radiation source were 0.3 m apart. Because the intensity of welding arc radiation depends on the intensity of welding current, the coefficients of light transmittance for a model of the filter were measured. Figure 10 illustrates the results of the tests for the developed model of the filter including the solution of 6-nitroBIPS in ethyl acetate.

The values of the light transmittance coefficients were within the limits defined for protection levels 9 and 10 for the developed model of the active welding filter. These values correspond to the guidelines on the selection of filters for welding with a covered electrode with current intensity between 100 and 125 A [19]. Average spectral coefficients of IR radiation transmittance and spectral UV transmittance were within the limits defined for protection level 10, too.

Photochromism is a nondestructive process but side reactions can occur. Oxidation is the main reason of the decomposition of photochromic dyes [4]. Samples of the filters were exposed

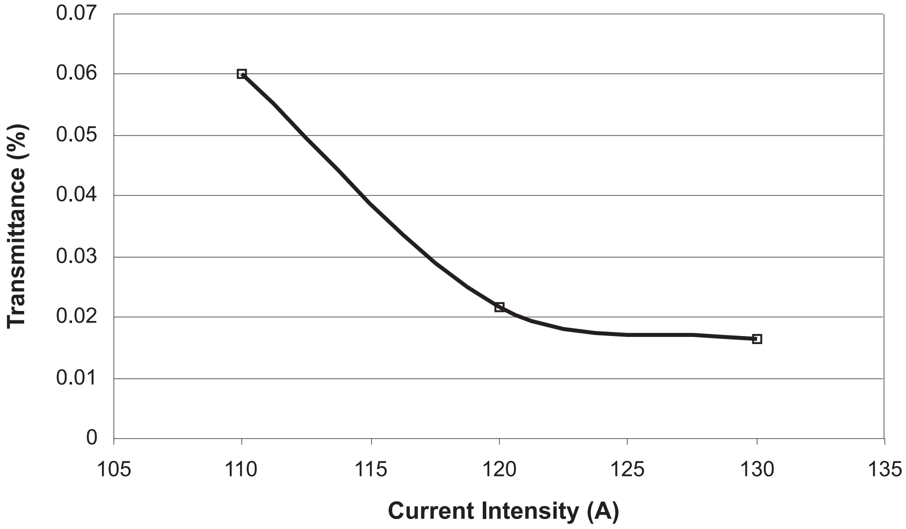

Figure 10. Dependence of the values of light transmittance coefficients on the welding current intensity with the filter and a radiation source 0.3 m apart.

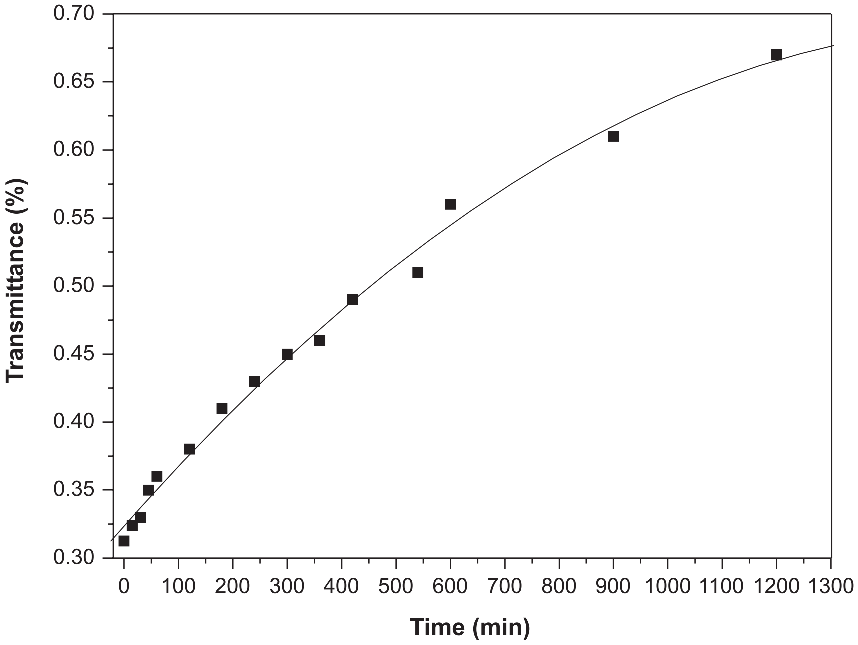

Figure 11. Fatigue of the welding filter during ultraviolet irradiation, fitted with a nonlinear function.

to irradiation with the intensity of 60 ± 1 klx. Transmittance measurements were conducted at illumination of 50 ± 1 klx, using a high pressure UV lamp. Transmittance spectra were collected with a Cary 5E spectrophotometer (Varian, Australia) fitted with a fiber optic accessory. The test results are shown in Figure 11.

The results showed that, if considering filter durability, a solution of 6-nitroBIPS in ethyl acetate was much better than a solution in other organic solvents. Switching time of the active welding filter was measured using a digital storage oscilloscope and a flash lamp as an irradiation source. Calculated switching time of the active welding filter was 0.011 ± 0.002 ms, so the filter's reaction time met the requirements of Standard No. EN 379:2003 [3].

5.5. SUMMARY

Spirobenzopyranoindolins have a great potential in optics devices, e.g., as in optical filters [5], principally because of their physical and chemical properties. Particularly the photophysical and photochemical properties of 1',3',3'-trimethyl-6-nitrospyro[2H-1-benzopyran-2,2'-indole]—absorption spectra, high quantum yield of photoisomerization and fluorescence lifetime—make it possible for this dye to be used in active welding filters.

Tests proved the developed model of an active welding filter with photochromic layer met the requirements of EN standards.

- Transmittance values obtained for an interference filter with a band of 40 nm was within the limits specified for protection level 5 in the light state (light transmittance coefficient in the 1.2–3.2% range), which ensure sufficient visibility of the welded object making precise welding possible.
- The changes in light transmittance coefficient of a filter with a solution of a photochromic dye in ethyl acetate were within the limits specified in Standard No. EN 169:2002 [19] for protection levels 9 and 10 (light transmittance coefficient in the 0.0610–0.0085% range). The light transmittance coefficients of this filter also comply with the guidelines on the selection of welding filters for welding with a covered electrode with current intensity between 100 and 150 A [19].
- Switching time of the filter 0.011 ms guarantees effective eye protection against the harmful effects of light glare [2, 3].

Furthermore, the tests showed that 6-nitroBIPS had the highest resistance to UV radiation when dissolved in ethyl acetate.

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