

Determining Ultraviolet Degradation of High-Visibility Warning Clothing With Photochromic Indicators

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The main purpose of this study was to select an appropriate photochromic dye and to develop a series of photochromic indicators showing ultraviolet (UV) degradation of selected background materials made from different polymers. The photochemistry of a series of photochromic compounds of oxazine and diarylethenes in thin polystyrene films were studied with spectroscopic methods. This paper also discusses the design and results of tests of UV photochromic indicators for high-visibility clothing.

photochromic indicators UV degradation warning clothing oxazine diarylethene

1. INTRODUCTION

According to available statistical data, 2.98 million people in Poland work outdoors, particularly in construction, agriculture and forestry [1]. Most of them have to use high-visibility warning clothing. During work, they are exposed to natural ultraviolet (UV) radiation. The intensity and frequency of this exposure differ depending on the group of workers, season and weather [2].

The degradation of personal protective equipment (PPE), and especially the bleaching of background materials for high-visibility warning clothing, is an important effect of exposure to natural UV radiation. As a result, the visibility of the users of such clothing may decrease even below the lower limits in Standard No. EN 471:2003+A1:2007 [3]. This process is particularly dangerous for PPE users because it is difficult to determine the degree of fading over time.

The problem of warning clothing ageing has been studied with simulation methods [4, 5, 6]. The most common destruction factors are sun radiation, oxygen and water. Exposing textiles to UV

radiation causes photochemical reactions, resulting in a loss of mechanical and chemical resistance of these materials. Moreover, dyes used in materials fade. In particular, UV radiation produced by the sun ages textiles. According to Łęzak and Frydrych, the dynamics of colour changes in fluorescent fabrics used in warning clothing depend on the spectrum of the radiation wave, radiation intensity, duration of exposure and humidity [4].

Simple indicators informing the user about the necessity to discard deficient high-visibility clothing could solve this problem efficiently. This study aimed to select a photochromic dye and to develop photochromic indicators to indicate degradation of selected background materials made from different polymers.

“Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms ... having different absorption spectra” (p. 642) [7]. The most prevalent organic photochromic systems involve unimolecular reactions. Usually, photochromic molecules have a colourless or pale yellow ground state form and a

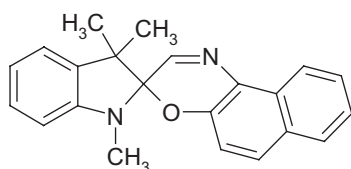
This paper was based on the results of a research task carried out within the scope of the first stage of the National Programme “Improvement of safety and working conditions” partly supported in 2008–2010—within the scope of research and development—by the Ministry of Science and Higher Education/National Centre for Research and Development. The Central Institute for Labour Protection – National Research Institute was the Programme’s main co-ordinator.

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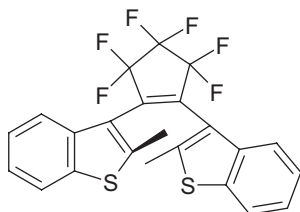
coloured excited form (e.g., red or blue). Photochromism and the subsequent thermal relaxation processes of many different organic dyes have been widely investigated, e.g., in spiropyranoindolines, spirooxazines, chromenes, fulgides, fulgimides and diarylethenes [5].

We used spectroscopic methods to study the photochemistry of a series of photochromic compounds of oxazine and diarylethenes in thin polystyrene films: (a) 1,3,3-trimethylspiro[indoline-2,3'-3[H]naphthyl[2,1-b][1,4]oxazine; (b) 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene and (c) 1,2-Bis(2,4-dimethyl-5phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (Figure 1).

(a)



(b)



(c)

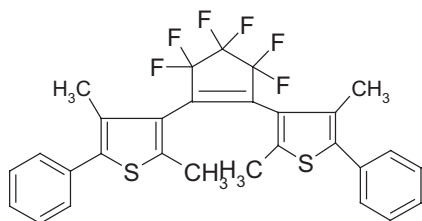


Figure 1. Series of photochromic compounds: (a) 1,3,3-trimethylspiro[indoline-2,3'-3[H]naphthyl[2,1-b][1,4]oxazine; (b) 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene and (c) 1,2-Bis(2,4-dimethyl-5phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene.

2. MATERIALS

Background materials for high-visibility warning clothing were bought from Polish manufactures.

Two types of knitted fabric made from orange and yellow polyester and two types of woven fabric made from orange and yellow cotton-polyester were tested. Table 1 presents the characteristics of those fabrics.

TABLE 1. Characteristics of Investigated Fabrics

Sample	Content	Mass per Square Metre (g/m ²)
1	100% polyester knitted fabric, disperse dye orange SEL-EN	140
2	100% polyester knitted fabric, disperse dye yellow SEL-8G	140
3	20% cotton 80% polyester woven fabric, disperse dye orange SEL-EN	285
4	20% cotton 80% polyester woven fabric, disperse dye orange yellow SEL-8G	285

Photochromic dyes (oxazine and diarylethenes) were bought from TCI Europe (Germany). The photochromic compounds were over 98% pure. The solvents (from Sigma-Aldrich, Germany) were high-performance chromatography-grade liquids and were used as supplied, without further purification.

3. EXPERIMENTAL METHODS

The reflectance of background materials were measured with a Mini Scan XE reflectometer (Hunter Lab, USA), with a measuring geometry of 45/0. Reflectance was measured after each 8-h cycle of UV exposure of the background materials. Tristimulus values were calculated with illuminant D65 and 2° standard observer data, in accordance with Standard No. EN 471:2003+A1:2007 [3, 6, 7].

The experiments were conducted until the chromacity co-ordinates *xy* were inside the quadrangles specified in Standard No. EN 471:2003+A1:2007 for red, orange-red and yellow [3]. Once these values are exceeded, materials lose their optical properties.

Irradiation was measured with a Gigahertz Optics (Germany) X2000 dosimeter during the exposure of the background materials to natural

and artificial UV radiation and to a xenon lamp mounted in a Xenotest 150 S+ unit (Atlas Material Testing Technology LLC, USA).

Photochromic dyes in polystyrene films were exposed to UV radiation in 8-h cycles. After those cycles, the absorption spectra of the photochromic dyes were obtained with a CARY 5000 spectrophotometer (VARIAN, USA). The change in colour during UV irradiation of the photochromic dyes was measured for specific wavelengths corresponding to maximum absorption of the dyes with an HR 2000 spectrometer (Ocean Optics, USA). Open forms of the photochromic dyes were induced with an OSRAM (Germany) HBO 450W/4 high pressure xenon lamp. Experiments were conducted until the absorption of photochromic dyes in polystyrene films for certain wavelengths fell under 0.1. Visual assessment showed that indicators faded for these absorption values.

4. DESIGN OF PHOTOCHROMIC INDICATORS

The concept of indicators showing the bleaching of background materials for high-visibility warning clothing follows using photochromic dyes to visualize UV degradation. Photochromic dyes have a colourless ground state form and a coloured excited form (e.g., red or blue). Exposing photochromic dyes to UV radiation degrades photochromic reactions, which eventually results in no colour change. After irradiation causing degradation of the photochromic indicator, its colour changes to yellow. This colour change (from blue or red to yellow) informs the user about the necessity to discard the high-visibility clothing. Figure 2 shows an indicator of UV

degradation of background materials for high-visibility warning clothing. Such indicators can be attached to warning clothing with snap fasteners or sewn to the background material.

5. RESULTS AND DISCUSSION

5.1. Degradation of Background Materials

According to Standard No. EN 471:2003+A1:2007, chromacity co-ordinates xy of background materials for high-visibility warning clothing should be within the areas specified for red, orange-red and yellow [3].

Figure 3 shows the results of tests of bleaching selected materials during exposure to natural solar radiation. The results of tests of high-visibility clothing showed that UV radiation was the main factor which caused the bleaching of background materials, particularly in the range from 280 to 315 nm.

Table 2 shows values of solar ultraviolet B (UVB) irradiation causing the degradation of background materials.

TABLE 2. Values of Solar Ultraviolet B (UVB) Irradiation Causing Degradation of Background Materials for High-Visibility Clothing

Sample	Exposure (days)	Irradiation (J/m^2)
1	15	$4.33 \cdot 10^5$
2	19	$5.51 \cdot 10^5$
3	23	$6.66 \cdot 10^5$
4	55	$1.65 \cdot 10^6$

Notes. UV = ultraviolet.

Furthermore, tests on the bleaching of background materials with a xenon lamp mounted in a Xenotest were conducted. Table 3 presents the results of colour fastness tests (according to

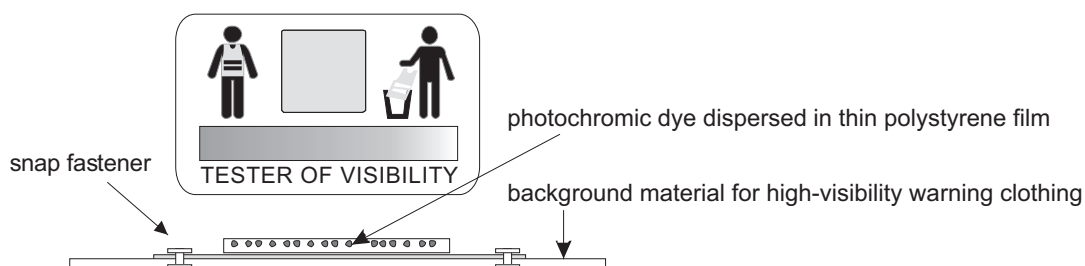


Figure 2. Indicators of ultraviolet degradation for background materials for high-visibility clothing.

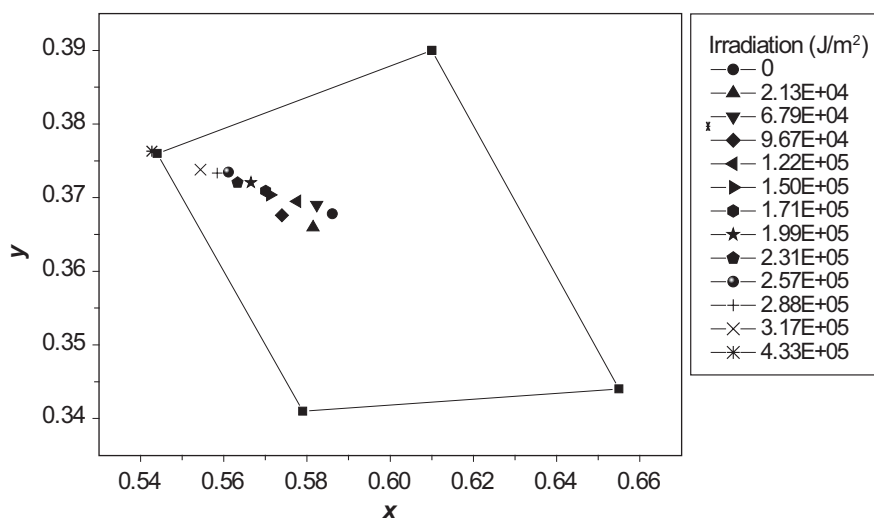


Figure 3. Change in tristimulus values for orange polyester knitted fabric depending on ultraviolet B (UVB) irradiation.

Standard No. EN 471:2003+A1:2007 [3]) for selected materials after irradiation in a Xenotest.

TABLE 3. Values of Ultraviolet B (UVB) Xenon Lamp Irradiation Causing Degradation of Background Materials for High-Visibility Clothing

Sample	Exposure (h)	Irradiation (J/m^2)
1	182	$4.42 \cdot 10^5$
2	173	$4.22 \cdot 10^5$
3	253	$6.15 \cdot 10^5$
4	580	$1.70 \cdot 10^6$

The irradiation values causing the degradation of background materials obtained in solar and xenon lamp tests were mostly similar. The relative differences were

- 2.0% for sample 1;
- 7.7% for sample 3;
- 2.9% for sample 4.

However, the relative difference for sample 2 was 23.4%. Solar irradiation causes faster degradation than irradiation from a xenon lamp. The differences in the radiation spectrum of the sun and a xenon lamp might be the cause of this phenomenon.

Moreover, an analysis of data on UV degradation of selected background materials showed that yellow cotton-polyester woven fabric was over threefold more resistant to UV degradation (which corresponds to 55 sunny working days)

than orange polyester knitted fabric. Taking into account the similarity of the results with solar and xenon irradiation for samples 1, 3 and 4, irradiation from a xenon lamp was used to test photochromic indicators.

5.2. Results of Absorption Measurements

Figure 4 shows the reversible photochromic reaction of 1,3,3-trimethylspiro[indoline-2,3'-3[H] naphthyl[2,1-b][1,4]oxazine [8, 9]. Figure 5 presents normalized absorption spectra of 1,3,3-trimethylspiro[indoline-2,3'-3[H] naphthyl[2,1-b][1,4]oxazine in ground and excited states. Due to the absorption of UV radiation, this dye undergoes a reversible photochromic reaction leading to a blue excited state form.

Figure 6 shows the reversible photochromic reaction of 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene [10]. Figure 7 presents normalized absorption spectra of 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene in ground and excited states. This dye undergoes a reversible photochromic reaction resulting in a red excited state.

Figure 8 presents the reversible photochromic reaction of 1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene. Figure 9 shows normalized absorption spectra of

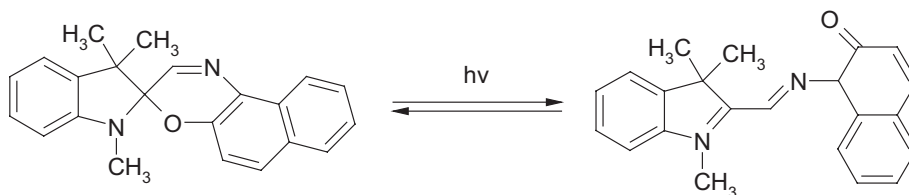


Figure 4. Scheme of the photochromic reaction of 1,3,3-trimethylspiro[indoline-2,3'-3[H]naphthyl[2,1-b][1,4]oxazine.

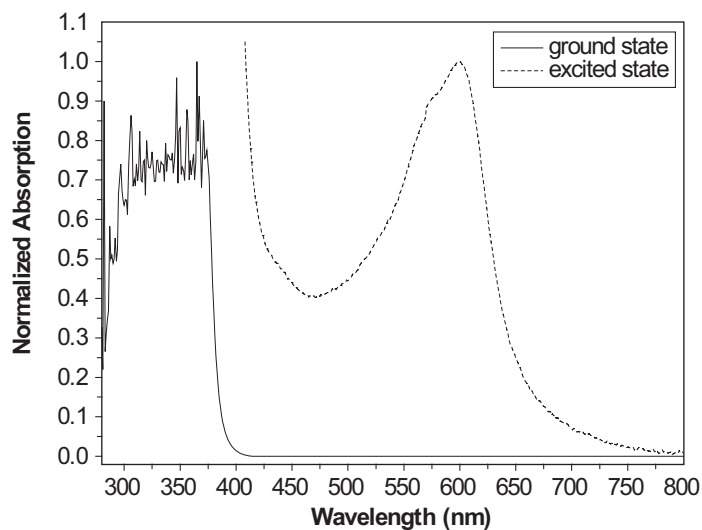


Figure 5. Normalized absorption spectra of 1,3,3-trimethylspiro[indoline-2,3'-3[H]naphthyl[2,1-b][1,4]oxazine in ground and excited states.

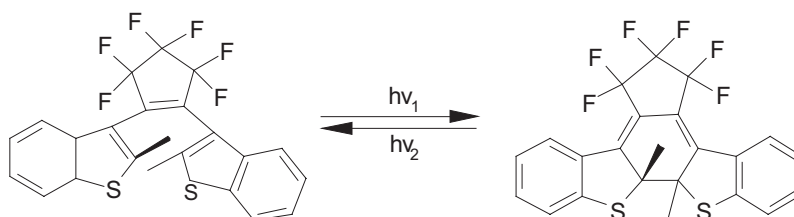


Figure 6. Scheme of the photochromic reaction of 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene.

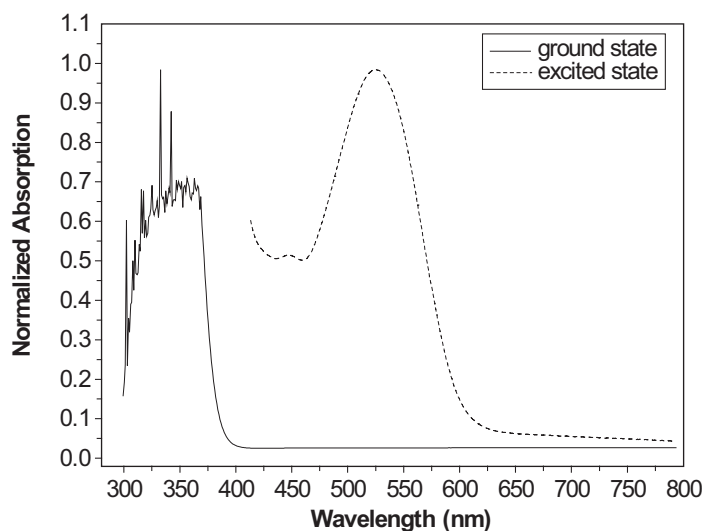


Figure 7. Normalized absorption spectra of 1,2-Bis[2-methylbenzo[b]thiophene-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene.

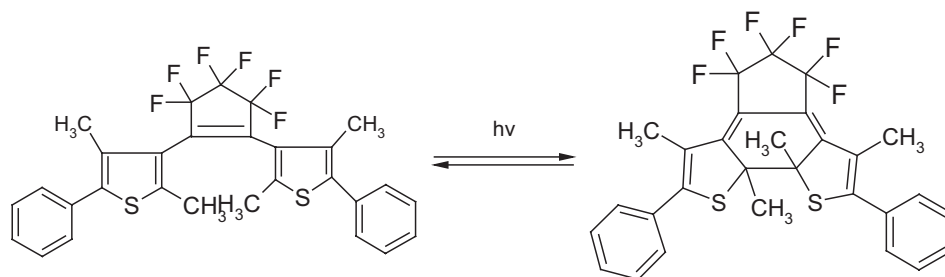


Figure 8. Scheme of the photochromic reaction of 1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene [10, 11].

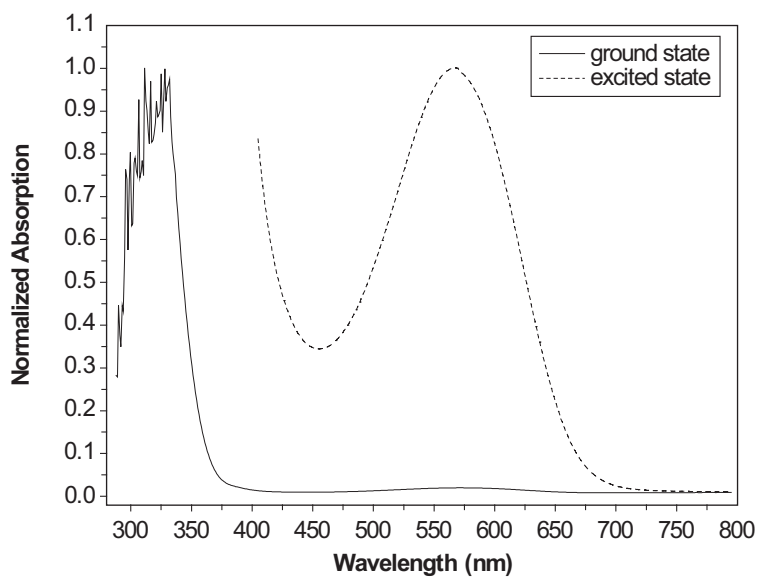


Figure 9. Normalized absorption spectra of 1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene in ground and excited states.

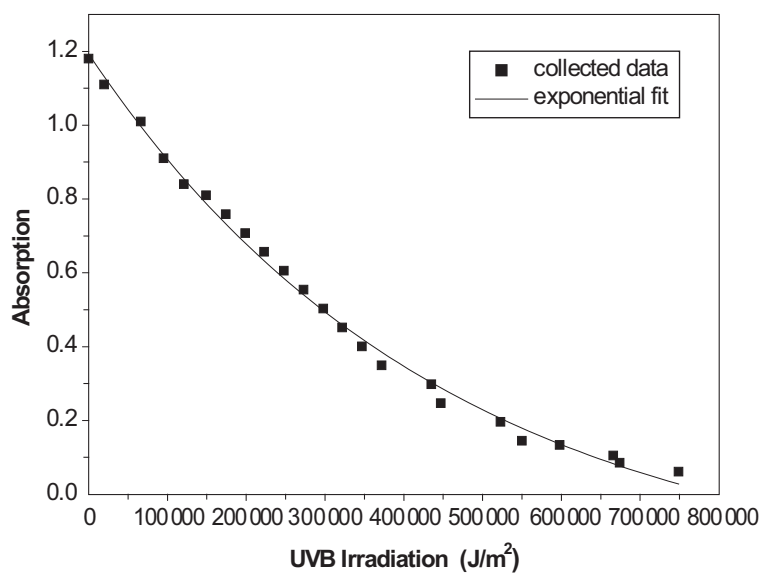


Figure 10. Change in absorption of 1,3,3-trimethylspiro[indoline-2,3'-3[H]naphthyl[2,1 b] [1,4] oxazine depending on ultraviolet B (UVB) irradiation.

1,2-Bis(2,4-dimethyl-5phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene in ground and excited states. The photochromic reaction of this dye leads to the development of a new absorption band in the visible spectrum (violet).

5.3. UV Degradation of Photochromic Dyes

This section presents the results of tests of polymer film photochromic indicators. The assumption was made that UVB radiation was the primary factor accountable for the degradation of photochromic dyes. Samples of polymer films containing selected photochromic dyes were exposed to UV radiation from a xenon lamp mounted in a Xenotest. Figure 10 shows the curve of the relationship between the absorption of 1,3,3-trimethylspirol[indoline-2,3'-3[H]naphthyl[2,1-b][1,4]oxazine measured for the 600-nm wavelength and total UVB irradiation.

An exponential function was found to fit the curve representing the dye fading over time. The assumption was made that the indicator faded permanently when absorption for a given wavelength fell below 0.1. Table 4 presents the resistance of selected photochromic dyes to UVB radiation.

TABLE 4. Results of Ultraviolet Resistance Tests for Selected Photochromic Dyes

Dye	Exposure (h)	Irradiation (J/m ²)
1	280	6.5·10 ⁵
2	650	1.62·10 ⁶
3	180	4.37·10 ⁵

Notes. Exposure to artificial ultraviolet radiation in a Xenotest.

A comparison of the relative difference in UVB irradiation values that caused degradation of photochromic indicators and selected background materials for high-visibility warning clothing showed that relative difference in UVB irradiation values for dyes dispersed in polystyrene film was

- 2.4% for dye 1 and sample 3;
- 1.8% for dye 2 and sample 4;
- 0.9% for dye 3 and sample 1.

6. SUMMARY

The irradiation values causing degradation of samples 1, 3 and 4 of background materials for high-visibility warning clothing and values obtained from xenon lamp tests were similar. Tests of UV resistance of photochromic dyes dispersed in polystyrene films showed that they could be used as degradation indicators for background materials for high-visibility warning clothing made from orange polyester knitted fabric and orange and yellow 20% cotton 80% polyester woven fabrics. The developed indicators designed to signal the necessity to discard PPE because of photochemical degradation will improve the safety of people working outdoors, particularly in road construction and other construction sectors.

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