Colorimetric Study on the Application of Some Fluorescent Naphthalimide Derivatives

P. Miladinova and T. Konstantinova*

Organic Synthesis Department, University of Chemical Technology and Metallurgy, 8 Ohridski str., Sofia 1756, Bulgaria

Abstract: Coloration of polyamide fabrics with five dyes naphthalimide derivatives was investigated. Three compounds, containing a tetramethylpiperidine (TMP) fragment were applied as fluorescent whitening agents (FWA). Materials with a bright color or whiteness and an intense fluorescence were obtained. The color characteristics using a Tristimulous colorimetry were recorded. The photo stability of the compounds in solution and on the polyamide fabrics was studied. It was found that among the dyes the compound 5 had the best photo stability. The FWA compounds, containing a stabilizer fragment in their molecule, had excellent stability in solution and very good stability on polyamide material.

Keywords: Naphthalimide dyes, fluorescent whitening agents, dyeing and whitening of polyamide, photo stability.

1. INTRODUCTION

Among various classical dyes, luminophores, due to their bright color and intense fluorescence, are of special interest. They were successfully applied for coloration of natural and synthetic materials [1, 2]. Recently, they have been widely applied in high technology such as solar energy sells, liquid-crystal displays, lasers, sensors and others [2, 3]. The fluorescent whitening agents (FWA) are also of special interest and have been applied not only for whitening of different materials but in high technology as well [3, 4]. The 1, 8-naphthalimide derivatives due to their bright color and intense fluorescence are well known as dyes for coloration of different materials, markers in biomaterials, sensors and others [3].

The stability of dyes and FWA was also of importance for their application. In the last years different approaches have been developed and different functional compounds have been synthesized [5, 6]. The possibility for "one-step" coloration and stabilization of polymers that we reported in the past few years was of special interest. In our papers we reported the synthesis of different dyes, including 1,8-naphthalimide derivatives, and their application for coloration of polymers [5-10]. It was of interest to study the color characteristics of the compounds synthesized and the possibility for their application for dyeing or whitening of textile materials. Some of the compounds under this present study contained a stabilizer (tetramethylpiperidine -TMP) fragment in their molecule, so it was of interest to investigate their photo stability and to compare it to the stability of the others. Therefore, this was the objective of the present study.

2. MATERIALS AND METHODS

2.1. Materials

The compounds under study were synthesized according to the method described before [11, 12]; polyamide fabrics (Polyamide 6) were a Bulgarian product (Agrochim, St. Zagora). All solvents were products of Merck (pro analysis or analytical grade).

2.2. Equipment and Methods

UV/Vis absorption spectra of the compounds were recorded in dimethyformamide (DMF; concentration $4x10^{-4}$ $g.mL^{-1}$) on a Hewlett-Packard 8452A UV/Vis spectrophotometer (2-nm resolution). Fluorescent spectra were measured on a Varian Eclipse fluorescent spectrophotometer in DMF ($4x10^{-4}$ $g.mL^{-1}$). The photo stability of the compounds was studied by irradiation of their DMF solutions in a Suntest equipment (Heraeus, Germany), fitted with an air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W/m^2). The process of their photo degradation was monitored colorimetrically (the standard calibration curve method), following the dependence of the compound's concentration on the time of irradiation, where the initial concentration of the compounds was accepted to be 100 %. Polyamide fabrics were dyed with the compounds **1-5** at concentration of 1 % on weight of fabric (o.w.f.) following the standard procedure [2, 13]. Materials with the compounds **6-8** at two concentrations 0.5 % and 1 % (o.w.f.) were treated [14]. The color characteristics of the dyed materials applying a Tristimulus Colorimetry (Data color technique) at three different illuminant light sources (a daylight - D65, a fluorescent light - CWF and an artificial light source with red-hot filament - A) were determined. The dyed or whitened fabrics thus obtained, were subjected to irradiation by UV light (wavelength λ_{max}= 290 nm) in a Suntest equipment.

3. RESULTS AND DISCUSSION

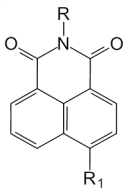
The compounds are presented by general formula I and II, where the meanings of R and R_1 are given.

The compounds **1-5** are yellow-orange in color with an intense greenish fluorescence in solution. The compounds **6-8** are colorless with an intense bluish fluorescence in solution under UV light.

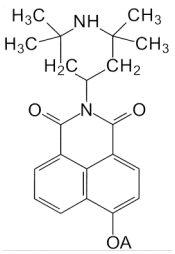
*Address correspondence to this author at the Organic Synthesis department, University of Chemical Technology &Metallurgy, 8 Ohridski str., Sofia 1756, Bulgaria; Tel/Fax: +3592-8163208;
E mail: konst@uctm.edu, temekonstantinova@abv.bg

1876-5203/10

Formula I



Formula II



1) R=-CH_3; R_1= -$NHNH_2$;

2) R=-$CH_2CH{=}CH_2$; R_1=-$NHNH_2$;

3) R=-$CH_2CH{=}CH_2$; R_1=-$NHCH_2CH_2NH_2$;

4) R=-CH_3 ; R_1=-$NHNHCOCH_2Cl$;

5) R=-$CH_2CH{=}CH_2$; R_1= -$NHNHCOCH_2Cl$

6) A= -CH_3;

7) A= -$CH_2CH{=}CH_2$;

8) A= -$CH_2CH_2OCOC(CH)_3{=}CH_2$;

3.1. Spectrophotometric Measurements

Firstly, it was of interest to study some of the spectral characteristics of the compounds, important for their application. The absorption UV/Vis and fluorescent spectra of the compounds in solution were recorded and the data obtained are presented in Table **1**.

Table 1. Spectrophotometric Data for the Compounds 1- 8*

Compound N	λ_{max} abs nm	log ε	λ_{max} fl nm
1	444	3.4	543
2	458	3.3	560
3	442	3.5	535
4	412	3.6	513
5	404	3.5	507
6	342 (356)	3.6	413
7	342 (356)	3.0	410
8	342 (356)	3.2	407

*DMF solutions with a concentration 4.10^{-4} $g.mL^{-1}$

One can see from these data that when the amino group in the hydrazine residue was acylated (compounds **4** and **5**), a hypso chromic shift in their absorption (46- 38 nm) and fluorescence λ_{max} (47 -28 nm) was observed. Nevertheless their absorption maxima remained in the visible region (they had a color). When in the fourth position of the naphthalimide ring an alcohol residue (methyl, allyl or HEMA) was involved (compounds 6-8), the λ_{max} of their absorption moved to the near UV region (342-356 nm). Their fluorescence was in the near visible one (407-413 nm), that was very important for their application as FWA.

3.2. Color Assessment

The polyamide samples with the compounds **1-5** were dyed and the color characteristics of the dyed materials applying a Tristimulus Colorimetry (Datacolor technique) at three different illuminant light sources were studied. Their reflectance spectra thus recorded are shown in Fig. (**1**).

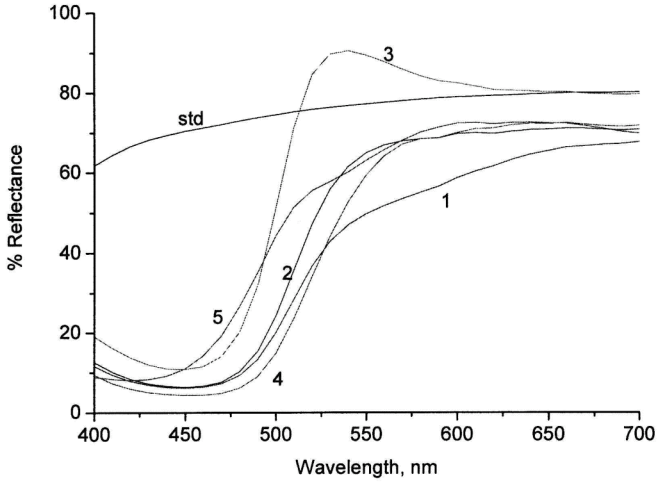


Fig. (1). Reflectance spectra of the dyed materials. **numbers of the curves correspond to the numbers of compounds; std: untreated polyamide fabric.*

One can see that the most intensive color with the compound **3** (-$NHCH_2CH_2NH_2$ group in the fourth position) was obtained. The acylation of the amino group in the hydrazine residue (compound **4**) affected (increasing) the hue of the dye compared to the compound **1**, but for the compound **5** (in comparison to compound **2**), neither increasing nor decreasing of the hue was observed. Similar measurements with polyamide materials treated with the compounds **6-8** were performed and the reflectance spectra of the whitened materials (Tristimulus Colorimetry-Data color technique) were recorded. In Fig. (**2**) the reflectance spectra of the compound **6** are presented. (The reflectance spectra for the compounds **7** and **8** were quite similar so we did not present them).

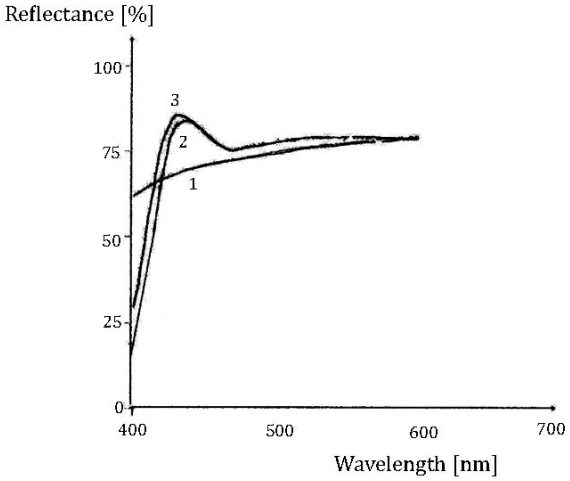


Fig. (2). Reflectance spectra of the polyamide materials. * *1- untreated polyamide; 2 - polyamide material treated with 0.5 % of compound 6; 3- polyamide treated with 1% of compound 6.*

Table 2. Tristimulous Data for the Compounds 1- 8 on Polyamide Fabrics[a]

Compound- concentration	WL	Purity (%)	x[b]	y[b]	L* [c]	a* [c]	b* [c]
1- 1 %	574	75.35	0.4570	0.4553	72.5	7.3	66.6
2- 1 %	572	77.88	0.4533	0.4680	79.2	2.9	75.7
3- 1 %	567	70.85	0.4179	0.4785	90.1	-12.4	75.7
4- 1 %	575	84.20	0.4796	0.4635	76.3	11.7	82.0
5- 1 %	570	65.08	0.4231	0.4527	81.5	-2.0	61.5
6- 0.5 %	-	-	0.3149	0.3306	91.1	0.7	0.1
6- 1%	-	-	0.3158	0.3324	90.9	0.3	0.9
7- 0.5 %	-	-	0.3302	0.3509	90.3	-1.1	9.9
7- 1%	-	-	0.3331	0.3530	90.6	-0.7	11.2
8- 0.5 %	-	-	0.3292	0.3511	90.4	-1.7	9.8
8 - 1%	-	-	0.3277	0.3482	90.5	-1.1	8.5
PA standard	571	5.68	0.3235	0.3412	90.3	0.03	5.4

[a] illuminant D_{65}, [b]- x and y chromaticity characteristics; [c] -L* (luminance), a* and b* - CIE coordinates.

These results showed that the application of the compound **6** (in both concentrations 0.5 and 1 %) led to a significant increasing of the light absorption value and from economical point of view, we considered that the concentration 0.5 % had to be recommended.

Applying the Tristimulous Colorimetry (Data color technique), some color characteristics of the materials treated with the compounds **1-8** were recorded. The results are presented in Table **2**.

One can see that the luminance L^* of the compounds was good. The color obtained with the compounds **1**, **2** and **4** had a reddish nuance (positive values of a^* and b^*), while that with the compounds **3** and **5** (positive b^* value and negative a^* value) had a greenish one.

3.3. Photo Stability of the Compounds

3.3.1. Photo Stability of the Compounds in Solution

In order to determine the photo stability of the compounds, their DMF solutions were irradiated by UV light in a Suntest equipment. As during the irradiation no change in their absorption (λ_{max}) was registered, the kinetics of photo degradation was monitored colorimetrically using the method of the standard calibration curve. The data obtained after 60 min of irradiation are presented in Table **3**.

These results showed that the compounds, containing a TMP fragment in their molecule (6-8) had the highest photo stability. The stability of the others was also good (50-60 % after 60 min of irradiation).

3.3.2. Photo Stability of the Compounds on Polyamide Fabrics

In order to determine the photo stability of the compounds on polyamide fabrics the materials dyed with the compounds 1-5 at a concentration of 1 % depth. (o.w.f.) or whitened with the compounds **6-8** at two concentrations 0.5 % and 1 % depth. (o.w.f.) were subjected to irradiation by UV light (wavelength λ_{max}= 290 nm) in a Suntest equipment. It was found that no change in the absorption maxima (λ_{max}) of the compounds during the irradiation was observed. They

Table 3. Concentration of the Compounds 1-8 During Irradiation*

Compound N	Concentration of the compound ** (%) after irradiation 15 min	Concentration of the compound** (%) after irradiation 30 min	Concentration of the compound** (%) after irradiation 60 min
1	75	70	65
2	68	64	60
3	62	59	56
4	70	65	60
5	72	65	62
6	100	99	98
7	99	99	98
8	99	99	98

*DMF solutions with concentration 4.10^{-4} $g.mL^{-1}$; **the concentration of each compound before irradiation was accepted 100 %.

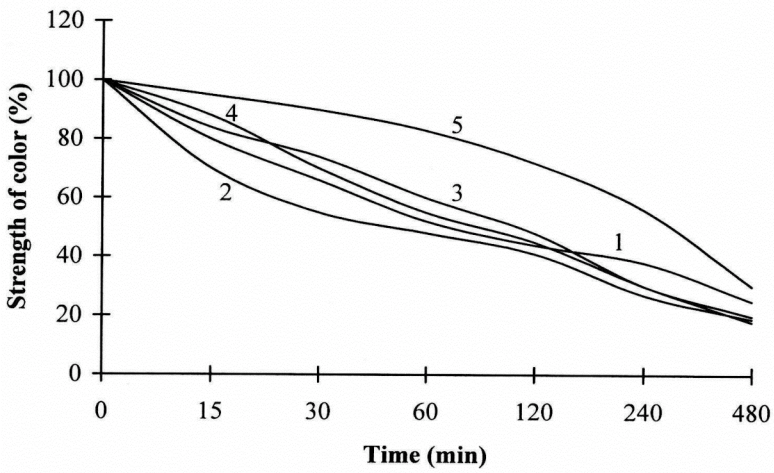


Fig. (3). Strength of color (%) as a function of time of irradiation (min) * *numbers on the curves correspond to the numbers of the compounds.*

were tested using the Tristimulous Colorimetry (Data color technique). The data for the compounds **1-5** obtained are presented in Fig. (**3**).

One can see from the figure that photo stability of the compound 5 is the highest (50 % degradation at 240th min). The stability of others was also good (≈ 50 % degradation after 120 min).

The similar experiments with the materials treated with the compounds **6-8** were performed. Materials with a bright whiteness and an intense bluish fluorescence were subjected to irradiation and then tested by Tristimulous Colorimetry (Data color technique). The data received are presented in Fig. (**4**).

We can see that the compound **6** had the highest photo stability at 0.5% concentration. This compound at 1 % and the compounds **7** and **8** at both concentrations (0.5 and 1%) degraded ≈ 50 % after 60 min. We consider that more detailed investigations in the future will enable us to determine the most suitable concentrations for application and their influence on the photo degradation process.

4. CONCLUSIONS

Based on the results of this study we can summarize that among the dyes (compounds **1-5**), the compound **5** can be recommended for coloration of polyamide fabrics, having good color characteristics and photo stability. The FWA (the compounds **6-8**) containing a TMP fragment in their molecule had very good photo stability and among them, the compound **6**, when was applied with 0.5 % concentration, can be recommended for whitening of polyamide materials.

ACKNOWLEDGEMENTS

Authors would like to thank the Science & Research Program of the University of Chemical Technology & Metallurgy, Sofia for the financial support.

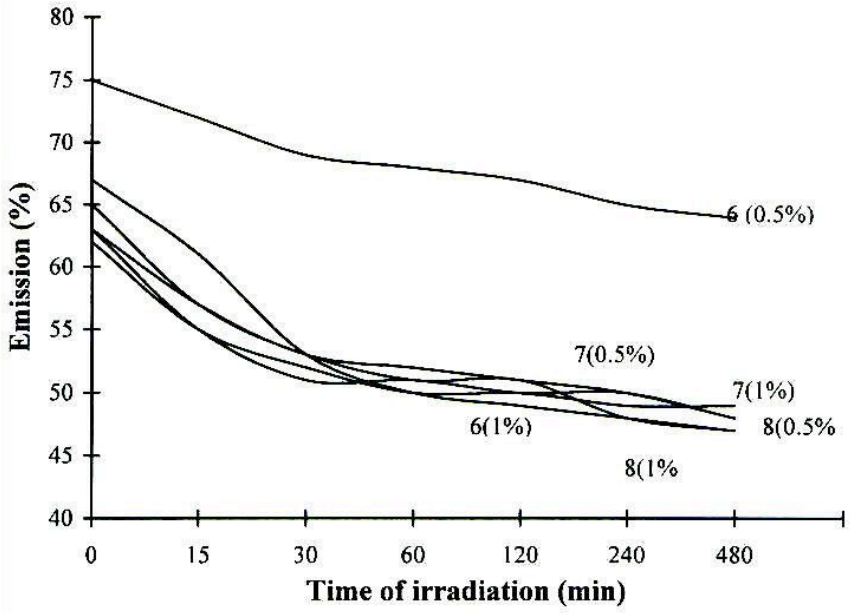


Fig. (4). Emission (%) as a function of time of irradiation (min) * *numbers on the curves correspond to the numbers of the compounds.*

REFERENCES

[1] H. Zollinger, *Color Chemistry,* VNC: Zurich, 1989.

[2] D.R. Warning and G. Hallas, Eds., *The Chemistry and Application of Dyes*, Plenum Press: London, 1990.

[3] P. Gregory, *High Technology Application of Organic Colorants,* Plenum Press: New York, 1991.

[4] R. Anliker and G. Müler, Eds., *Fluorescent Whitening Agents,* Georg Thieme Verlag: Stuttgart, 1975, pp. 51-52.

[5] T.N. Konstantinova and P.P. Miladinova, "Dyes and pigments with ecologically more tolerant application", In: *Dyes and Pigments-New Research,* A.R. Lang, Ed., Nova Science Publishers: New York, 2009, pp. 383-402.

[6] V.V. Bojinov, "Synergistic efficiency of combined HALS-UV absorber polymerizable stabilizers", *J. Appl. Polym. Sci.*, vol. 102, pp. 2408- 2415, March 2006.

[7] V.V. Bojinov and T.N. Konstantinova, "On the possibility of "one-step" coloration and stabilization of polystyrene", *Polym. Degrad. Stab.* vol. 68, pp. 295-298, April 2000.

[8] V.V. Bojinov and T.N. Konstantinova, "Synthesis of polymerizable 1, 8-naphthalimide dyes containing hindered amine fragment", *Dyes Pigm.*, vol. 54, pp. 239-245, September 2002.

[9] T.N. Konstantinova, R.D. Lazarova and V.V. Bojinov, "On the photo stability of some naphthalimide dyes and their copolymers with methyl methacrylate", *Polym. Degrad. Stab.*, vol. 82, pp. 115-118, January 2003.

[10] P.P. Miladinova and T.N. Konstantinova, **"**On the synthesis of some reactive triazine azodyes containing tetramethylpiperidine fragment", *Dyes Pigm.*, vol. 67, pp. 63-69, October 2005.

[11] T.N. Konstantinova and P.P. Miladinova, "Synthesis and properties of some fluorescent 1,8- naphthalimide derivatives and their copolymers with methylmethacrylate", *J. Appl. Polym. Sci.*, vol. 111, pp. 1991- 1998, February 2009.

[12] T.N. Konstantinova, A.B. Spirieva and T.I. Petkova, "The synthesis, properties and application of some 1,8-naphthalimide dyes", *Dyes Pigm.*, vol. 45 pp. 125-129, May 2000.

[13] R.I. Betcheva, T.N. Konstantinova and A.B. Spirieva, "Colorimertic study on the textile application of some benzanthrone dyes", *Fibres Text. East. Eur.*, N 2, pp. 41-44, July-September 2001.

[14] T.N. Konstantinova and I.K. Grabchev, "Aufhellen von Textilien mit neuen optischen Aufhellen", *Melliand Textilberichte*, vol. 75, pp. 125-127, February 1994.

Received: June 19, 2009 Revised: October 30, 2009 Accepted: March 03, 2010