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メタデータ	言語: English 出版者: 公開日: 2010-04-05 キーワード (Ja): キーワード (En): 作成者: Maruyama, Takehito, Kuroki, Nobuhiko, Konishi, Kenzo メールアドレス: 所属:
URL	https://doi.org/10.24729/00008935

Studies on the Fluorescent Brightening Dyes for Polyacrylonitrile Fiber

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(Received June 30, 1964)

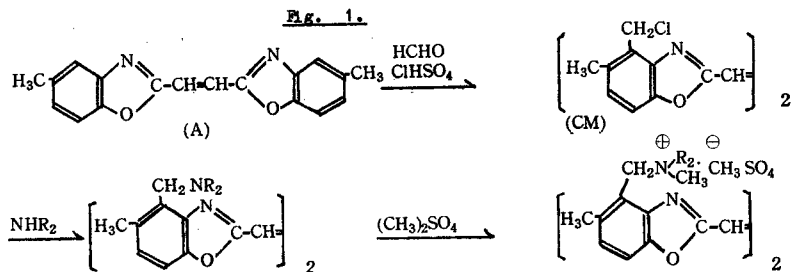
With a view that cationic dye as a class has affinity to polyacrylonitrile type fiber and α, β -bis (5-methylbenzoxazolyl-(2))-ethylene (A) is an excellent fluorescent brightening dye for polyester type fiber, A was directly chloromethylated and chlorosulfonated respectively, and these compounds were transformed into fluorescent brightening dye containing cationic group, such as $-\text{CH}_2\text{NR}_2$ and $-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NR}_2$ group. By introduction of such groups, the peak of absorption spectrum shifts towards longer wave-length in dimethylformamide, and the fluorescence disappears in the visible region. However, these compounds in an acidic aqueous solution, and corresponding quaternary salts, which were derived from the former compounds by treatment with dimethylsulfate, in water show a strong fluorescence, and their fluorescent maxima are observed at the same wave-length, 435 $m\mu$. Applicability and brightening effect of these compounds on several synthetic fibers (Vinylon, 6-nylon, acetate fiber and Cashimilon F (acrylic fiber with acid site)) were examined. The fluorescent decay of these brightened fabrics by arc lamp irradiation was measured. All these compounds, especially quaternary salt type compounds, by simultaneous use of sodium chlorite as a bleaching agent in a dye bath have an excellent brightening effect and fastness to light on Cashimilon F.

1. Introduction

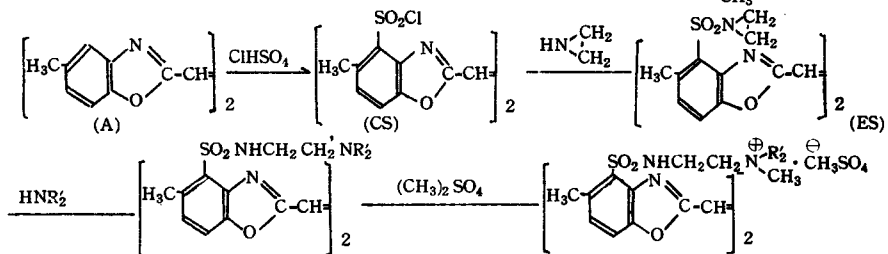
Textile material made from natural or synthetic fibers generally show a yellowish tinge due to the presence of certain colored impurities which absorb some of the incident light in the blue region. Removal of the yellowish tinge can be achieved by removal or destruction of the coloring matter itself by chemical treatments, addition of bluing dyes which absorb the yellow light and thereby bring down the level of light reflected in this region to that of the blue range, and treatment with certain organic compounds (fluorescent brightening dyes) which have the capacity of absorbing light in the ultraviolet region of the spectrum of daylight or artificial light and re-emitting it as light in the blue region of the visible spectrum.

The first commercial fluorescent brightening dyes contain as the fluorophore 4,4'-diaminostilbene-2,2'-disulfonic acid. This group provides a part of a linear chain required for affinity for cellulose. But they have not sufficient affinity for acetate, nylon and other synthetic fibers. Though during the past few years a large number of various types of fluorescent brightening dyes for synthetic fibers have been synthesized and marketed, almost these dyes have a same serious defect, that the light fastness of these dyes is not adequate to practical application. Especially, for polyacrylonitrile fiber, fluorescent brightening dye having excellent fastness to light has not been found. Recently, it has been found that cationic dyes show good affinity for acrylic fiber under slightly acidic

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Dye No.	-NR ₂	Dye No.	$\oplus \text{R}_2$ -N ⁺ -CH ₃
1	-N(C ₂ H ₅) ₂	1'	\oplus -N-(C ₂ H ₅) ₂ CH ₃
2	-N(C ₂ H ₄ OH) ₂	2'	\oplus -N-(C ₂ H ₄ OH) ₂ CH ₃
3		3'	\oplus
4		4'	\oplus
5		5'	\oplus



Dye No.	-NR ₂	Dye No.	$\oplus \text{R}_2$ -N ⁺ -CH ₃
6	-N(C ₂ H ₅) ₂	6'	\oplus -N-(C ₂ H ₅) ₂ CH ₃
7	-N(C ₄ H ₉ -n) ₂	7'	\oplus -N-(C ₄ H ₉ -n) ₂ CH ₃
8	-N(C ₂ H ₄ OH) ₂	8'	\oplus -N-(C ₂ H ₄ OH) ₂ CH ₃
9		9'	\oplus
10		10'	\oplus
11		11'	\oplus

dyeing conditions, and the fastness to light of these dyeings is significantly better than that of the same dyes on tannin-mordanted cotton¹⁾.

In the previous paper, one of present authors (Knoishi) reported that, α,β -bis (5-methylbenzoxazolyl-(2))-ethylene containing cationic group, such as methylpyridinium, picolinium and so on, showed excellent brightening effect and fastness to light on acrylic fiber²⁾. This fact suggests the result of above-mentioned observation on coloring matter is applicable to the case of fluorescent brightening dyes. From this point of view, in this paper several fluorescent brightening dyes containing cationic group for acrylic fiber were synthesized.

The synthetic processes and structures of these dyes are represented in Fig. 1.

As expected, these dyes show excellent brightening effect and fastness to light on acrylic fiber.

2. Experimental

2.1 Preparation of Fluorescent Brightening Dyes containing N-substituted Aminomethyl Group

2.1.1 α,β -bis(4-chloromethyl-5-methylbenzoxazolyl-(2))-ethylene (CM) Chlorosulfonic acid (58 g) is added at 10°C to the mixture of 6 g of formaldehyde and 30 ml of sulfuric acid (d. 1.84) and to the resulting solution is added with stirring 5 g of α,β -bis (5-methylbenzoxazolyl-(2))-ethylene (A). The mixture is kept at 60°C for 48 hours with stirring, and after cooling it is poured on to 500 ml of ice water. The precipitate thus obtained is collected and washed with ice water, and then dried at 60-80°C. It is extracted with 200 ml of chlorobenzene, and the chlorobenzene solution is distilled under reduced pressure. The crude product melts at 250-270°C. Following analytical results show that this crude product is dichloromethyl derivative of A.

Calc'd for dichloromethyl deriv.	(N % 7.24, C % 62.07, H% 4.14, Cl % 18.32)
Found	(N % 7.42, C % 62.40, H % 4.56, Cl % 18.14)

This product is purified by repeated crystallization from chlorobenzene, m.p. 292°C.

2.1.2 α,β -bis(4-diethylaminomethyl-5-methylbenzoxazolyl-(2))-ethylene (No. 1)

Diethylamine (5 g) is added slowly to the mixture of 5 g of CM compound (m.p. 250-270°C) obtained above and 40 ml of chlorobenzene. After the amine was added, the mixture is steam distilled to remove chlorobenzene. The residue, insoluble in water, is collected and washed with a small amount of isopropyl alcohol. The crude product (4.8 g), m.p. 160-170°C is obtained, and purified by repeated crystallization from dioxane with active carbon, m.p. 174-5°C.

Compounds (Nos. 2-5) were prepared by the same procedure as mentioned above from CM compound and dihydroxyethylamine, piperidine, α -pipercoline and morpholine, respectively. The melting points and yields of crude and pure compounds are summarized in Table. 1.

Table 1.

Dye No.	Crude Product		Pure Product		Analysis					
	m.p. (°C)	Yield (%)	m.p. (°C)	Yield (%)	N		C		H	
					Found	Calc'd	Found	Calc'd	Found	Calc'd
1	160-170	80	174-175	67 ^{a)}	12.44	12.17	72.86	73.04	7.92	7.83
2	150-160	78	185-186	54 ^{b)}	11.01	10.69	64.30	64.12	7.04	6.87
3	200-220	80	224-227	65 ^{c)}	11.71	11.57	73.65	74.38	7.55	7.44
4	180-200	83	216-220	64 ^{c)}	11.06	10.94	74.76	75.00	7.99	7.81
5	170-200	86	217-219	47 ^{c)}	11.24	11.48	—	68.85	—	6.56

a) Recrystallized from isopropyl alcohol/dioxane

b) Recrystallized from methyl alcohol/dioxane

c) Recrystallized from dioxane

2.1.3 Quaternization with dimethylsulfate (Nos. 1'-5')

A slight excess of dimethylsulfate is added to a solution of 1 g of above obtained aminomethyl derivative in 20 ml of benzene. The yellowish fluorescent crystal soon commences to separate. The reaction is completed by raising the temperature gradually and finally heating under reflux on a water bath for 2 hours. The crystal is collected and dried in vacuum desiccator over concentrated sulfuric acid. The yield is almost quantitative. The sintering points and the shades of the fluorescence under black light of these quaternary salts are given in Table. 2.

Table 2.

Dye No.	S.P. (°C)	Analysis (N %)		Shade of Fluorescence
		Found	Calc'd	
1'	214-218	7.13	7.86	Pale Yellow
2'	245-250	6.57	7.22	Reddish Yellow
3'*	240-242	6.95	6.42	Bright Yellow
4'	194-199	7.05	7.33	Bright Yellow
5'	194-198	7.51	7.57	Bright Yellow

* ZnCl₂ double salt

S.P.=Sintering Point

2.2 Preparation of Fluorescent Brightening Dyes containing N-substituted Aminosulfamoyl Group

2.2.1 α,β -bis(5-methyl-X-chlorosulfonylbenzoxazolyl-(2))-ethylene (CM)

Compound A (5 g) is added slowly into 50 g of excess chlorosulfonic acid at below 40°C. After all compound has been dissolved, the stirring is continued for 5 hours at 120-130°C. The clean solution is then poured upon chipped ice, the precipitate is collected, washed with ice water and dried in vacuum desiccator over phosphorous pentoxide. Yield is about 7 g.

2.2.2 α,β -bis(5-methyl-X-N-ethylenesulfamoylbenzoxazolyl-(2))-ethylene (ES)

CS compound (7 g)-finely powdered and dried-is added to the solution of 2.5 g of ethyleneimine, 60 ml of acetone and 2 g of potassium carbonate in 10 ml of water. The mixture is stirred at below 5°C for 2 hours, and poured onto 150 ml of ice water. The product is collected, washed with ice water and dried in vacuum desiccator over phosphorous pentoxide m.p. above 360°C. Yield is about 7 g.

2.2.3 α,β -bis(5-methyl-4-N-diethylaminosulfamoylbenzoxazolyl-(2))-ethylene (No. 6)

Diethylamine (3.7 g) (5/100 mole) is added slowly to the mixture of 5 g of ES compound (1/100 mole) and 500 ml of acetone at room temperature. When all amine has been added the mixture is boiled for 1 hour. The reaction mixture is filtered and the filtrate is distilled to remove acetone in reduced pressure. The residue is washed with a small amount of ethyl alcohol. Crude product (2.5 g), m.p. 224-230° C, is obtained and purified by crystallization with acetic acid several times, m. p. 235°C. Compounds (Nos 7-11) were prepared by the same procedure as mentioned above from ES compound and di-n-butylamine, dihydroxyethylamine, piperidine, α -pipercoline and morpholine, respectively. Their melting points and yields of crude and pure products and results of analysis are shown in Table 3.

Table 3.

Dye No.	Crude Product		Pure Product		Analysis			
	m.p. (°C)	yield (%)	m.p. (°C)	yield (%)	N %		S %	
					found	calc'd	found	calc'd
6	224-230	50	234-235	16 ^{a)}	12.57	13.00	9.75	9.91
7	30- 40	74	47.5- 50	20 ^{b)}	10.50	11.08	8.23	8.44
8	210-220	36	224.5-227.5	24 ^{b)}	11.09	11.83	8.67	9.01
9	195-210	50	226-230	21 ^{b)}	12.41	12.54	9.32	9.55
10	210-225	53	235-237	20 ^{a)}	11.72	12.03	8.85	9.17
11	112-130	62	220-226	14 ^{c)}	11.86	13.46	8.96	9.49

a) crystallized from acetic acid b) crystallized from aqueous acetic acid
c) crystallized from ethyl alcohol.

2.2.4 Quaternization with dimethylsulfate (Nos. 6'-11')

The procedure of quaternization was carried out by the same method as those described in the 2.1.3. The yield in each case was 80-90 %. The sintering points, decomposition points and shades of the fluorescence of these salts are shown in Table 4.

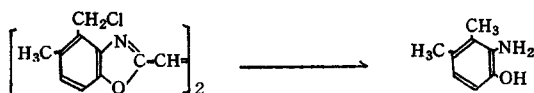
Table 4.

Dye No.	S.p. (°C)	D.p. (°C)	Analysis (N %)		Shade of fluorescence
			found	calc'd	
6'	265	271	9.32	9.35	Pale Yellow
7'	143	149	6.92	7.33	Yellow
8'	259	269	8.42	8.73	Pale Yellow
9'	215	270	8.75	9.11	Yellow
10'	220.5	273.5	8.51	8.84	Yellow
11'	80	129	8.49	9.07	Reddish Yellow

2.3 Determination of the substituted position of cationic group on these dyes

By treatment with zinc amalgam in hydrochloric acid, the CM compound (m.p. 292°C) was converted to the corresponding amino phenol as shown in Fig. 2.

Fig. 2.



This aminophenol derivative was proved to be identical with authentic 2-amino-3,4-dimethylphenol, which is prepared through another route, by mixed melting point method. From this result, it was suggested that the chloromethyl group was introduced for the most part to the 4,4' position in α,β -bis (5-methylbenzoxazolyl-(2))ethylene (A)².

Furthermore, infrared spectra of N-diethylaminomethyl derivative (No. 1) derived from CM compound, N-diethylamino sulfamoyl derivative (No. 6) derived from ES compound were measured by KBr method, and compared with that of original compound A. The strong absorption band at 860 cm^{-1} arising from the presence of one isolated ring hydrogen atom in benzene ring (out-of-plane CH deformation vibration) for compound A disappeared in the case of compound No. 1 and No. 6. From these results, we conclude that N-substituted disulfamoyl group in these dyes also exists in a same position as above-mentioned N-substituted diaminomethyl group.

2.4 Fluorescent brightening procedure

The cloths used for the brightening treatment were 100 % 6-nylon, Vinyon, acetate and Cashimilon F (polyacrylonitrile with acid site), the liquor ratio being 50:1 and the dye being 0.2 % on the weight of fiber.

2.4.1 Vinyon, 6-nylon and acetate; The dye (quaternary salt type) was dissolved in distilled water with Emalgen 913 (nonionic dispersing agent, Kao-Atlas Co.Ltd.). The fabric was dyed at about 80°C for 1 hour.

2.4.2 Cashimilon F; a) The dye was dissolved in distilled water containing acetic acid (10ml/1), and dyed on the Cashimilon F at about 100°C for 1 hour.
b) Sodium chlorite (5g/1) was added to the dye solution containing acetic acid (10ml/1). Optical and chemical bleaching were simultaneously carried out.

2.5 Measurement of spectra

Absorption maxima were determined with a Hitachi Spectrophotometer Type EPS-2U in solution at room temperature. Extinction coefficients are calculated by dividing the molar cell concentration. These dyes in solution and on fabrics were excited by monochromatic radiation ($365\text{ m}\mu$) with a Hitach Fluorescent Attachment, and fluorescent emission spectra were observed with a Hitach Spectrophotometer EPS-2U.

2.6 Indication of Brightening Result

2.6.1 Assessment of brightening efficiency This was estimated as 5 for dyeings having excellent efficiency of whitening by the visual evaluation under xenon lamp (Toshiba Standard Daylight, type SWI-300), and good as 4 and estimated as 3, 2 and 1 with decrease of whitening effect.

Simultaneously, the fluorescent maximum and relative intensity of these dyes on fabrics obtained by spectrometry was listed in Table 6,

2.6.2 Lightfastness The fastness to light is determined by comparing with the decay of fluorescent intensity of these dyes on fabric pieces at each maximum emission wavelength during the irradiation with a carbon arc lamp of Toyo Rika Co's. Fade Meter Model FA-1. The values of relative intensity (initial intensity of each sample being taken as 100) at various exposure times (1, 2 and 5 hours) were shown in Table 7.

3. Results and Discussion

3.1 Spectral Property of the Brightening Dyes

It has been found that the starting material A and its-CH₂OR and-SO₂NR₂ derivatives showed a yellow fluorescence on the solid state under black light^{(3), (4)}.

However, the fluorescence of compounds containing tertiary aminogroup (Nos. 1-11) disappears on the solid state or in organic solvent (dimethylformamide). On the other hand, in an acidic aqueous solution their fluorescent spectra appear in the visible region. Quaternary salts (Nos. 1'-11') show a yellow fluorescence on the solid state (Table 2),

Table 6. Absorption and Fluorescent Results.

Dye No.	(Solvent; acetic acid/water=4 ml/l)				(Solvent; Dimethylformamide)		
	Absorption Maximum		Fluorescent Maximum		Absorption	Maximum	Fluorescent Maximum
	λ_{\max} (m μ)	ϵ_{\max} (10 ⁴)	(m μ)	I*	λ_{\max} (m μ)	ϵ_{\max} (10 ⁴)	
1	368	4.46	435	100	367	4.30	none
2	368	4.40	435	104	367	4.34	none
3	368	4.46	435	103	367	4.41	none
4	368	4.67	435	107	367	4.22	none
5	368	4.51	435	103	367	4.32	none
6	373	5.05	435	112	375	4.40	none
7	370	4.55	435	80	373	4.28	none
8	373	5.04	435	102	374	4.42	none
9	373	4.35	435	103	375	3.97	none
10	373	4.87	435	106	375	4.31	none
11	370	4.65	435	95	373	3.98	none

Dye No.	(Solvent: Water)			
	Absorption Maximum		Fluorescent Maximum	
	λ_{\max} (m μ)	ϵ_{\max} (10 ⁴)	(m μ)	I*
1'	370	4.59	435	111
2'	370	4.44	435	102
3'	370	4.45	435	106
4'	370	4.99	435	115
5'	370	5.08	435	97
6'	373	4.97	435	87
7'	370	3.76	435	78
8'	373	4.49	435	87
9'	373	4.57	435	98
10'	373	4.72	435	93
11'	372	4.46	435	78

I* = Relative fluorescent intensity

(Table 4) and are easily soluble in water. These solutions have a strong blue fluorescence. Absorption and fluorescent spectra of these dyes in solution are shown in Table 6. The relative intensity of each fluorescence is measured at same concentration (1×10^{-5} mole/l) and compared with that of compound No. 1 in acetic acid/water (4 ml/l), which is listed as 100.

The shapes of the spectra of these compounds are closely similar to that of the starting material, compound A. By introduction of $-\text{CH}_2\text{NR}_2$ group to A, the peak of absorption spectrum shifts about $5 \text{ m}\mu$ towards longer wave-length in DMF without any significant change in intensity (compound A; $\lambda_{\text{max}}=360 \text{ m}\mu$, $\epsilon_{\text{max}} \times 10^{-4}=4.31$).

By introduction of $-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NR}_2$ group, the shift of absorption maximum is particularly noticeable (about $15 \text{ m}\mu$). The tendency of these bathochromic shift is similar to that obtained in the previous papers^{3),4)}. That is, in the case of $-\text{CH}_2\text{OR}$ derivative of A, bathochromic shift was $5 \text{ m}\mu$, while in the case of $-\text{SO}_2\text{NR}_2$ derivative the shift was about $10 \text{ m}\mu$. On the other hand, tertiary amino compounds (Nos. 1-11) in an acidic aqueous solution, and quaternary salts (Nos. 1'-11') in water show a strong fluorescence, and their fluorescent maxima are observed at same wave-length, $435 \text{ m}\mu$.

3.2 Fluorescent Brightening Effect

It has been known that the fluorescence of dye on fabric reaches a limit at high concentrations. The reason is that almost all available ultraviolet energy used for exciting the fluorescence is absorbed at higher concentration, and additional fluorescent brightening dye cannot absorb it any more. Furthermore, in high concentration, the brightened fabric is sometimes tinged up in undesirable pale yellow by color of dye itself. Considering these behaviors, it is desired that the suitable concentration used for brightening of these fibers is determined. It is found that the range from 0.15 to 0.3 % on the weight of fiber is suitable. The details of the determination were reported in the previous papers^{5),6)}. In this paper, a result of brightening on several synthetic fibers summarized in Table 7 is obtained by brightening from bath containing brightening dye, 0.2 % on the weight of fiber.

When tertiary amino compounds (Nos. 1-11), which have not fluorescence on the solid state, have been dyed on Vinyon, 6-nylon and acetate from neutral bath, the fluorescence of these fabrics was not observed. Under acidic condition the fluorescence of these fabrics appears in the blue region.

On the other hand, Cashimilon F brightened with these dyes always have a fluorescence, even when the brightenings are immersed in an alkaline solution.

These facts suggest that these dyes would be absorbed mainly by electrostatic attraction on acidic group on Cashimilon F as is described in another report⁷⁾.

In this Table, the result on the relative intensity shows that these dyes containing cationic group possess more excellent affinity for acrylic fiber than for the other fibers.

However, in general, polyacrylonitrile fiber is accompanied with yellowing by treatment at high temperature, so that the brightened acrylic fiber thus obtained which has high intensity does not always show visually adequate brightening effect.

In fact, as shown in Table 7, the brightening effect with visual assessment of these

Table 7. Brightening Results.

Dye No.	(Cashimilon F)					
	Fluorescent Maximum (m μ)	Relative Intensity	Visual Assessment	with sodium chlorite (5 g/l)		
				Fluorescent Maximum (m μ)	Relative Intensity	Visual Assessment
1	440	57	1	430	58	5
2	442	36	1	430	32	4
3	440	60	1	430	58	5
4	440	66	1	430	67	5
5	440	27	1	430	27	3
6	437	68	1	430	75	5
7	436	43	1	430	72	5
8	437	59	1	430	67	4
9	437	55	1	430	52	4
10	437	48	1	430	62	4
11	437	29	1	430	31	4
1'	439	89	1	430	100	5
2'	438	69	1	430	85	5
3'	436	61	1	430	81	5
4'	440	63	1	430	76	5
5'	438	68	1	430	87	5
6'	436	60	1	430	92	5
7'	435	53	1	430	75	5
8'	437	57	1	430	69	5
9'	436	67	1	430	86	5
10'	437	49	1	430	92	5
11'	437	56	1	430	88	5

Dye No.	(Vinylon)			(acteate)			(6-nylon)		
	Fluorescent Max. (m μ)	Relative Int.	Visual Asses.	Fluores. Max. (m μ)	Relative Int.	Visual Asses.	Fluores. Max. (m μ)	Relative Int.	Visual Asses.
1'	430	73	5	430	73	4	—	7	1
2'	430	47	4	430	46	3	—	10	1
3'	430	45	3	430	53	3	—	7	1
4'	430	60	4	430	55	3	—	4	1
5'	430	56	4	430	58	4	—	5	1
6'	430	54	3	430	56	3	—	5	1
7'	430	47	3	430	32	2	—	10	1
8'	432	52	3	430	53	3	—	10	1
9'	432	61	3	430	29	2	—	7	1
10'	432	58	3	430	25	2	—	10	1
11'	432	54	3	430	22	2	—	5	1

dyes on acrylic fiber is not observed in spite of relatively high intensity of the fabrics, but when the brightening dyes are used together with sodium chlorite as a bleaching agent, the brightening effect can be increased considerably. These dyes, especially quaternary salt type dyes (Nos. 1'-11'), have in a dye bath excellent brightening effect by the simultaneous use of sodium chlorite,

3.3 Lightfastness

The lightfastness of these dyes on Vinylon, 6-nylon and acetate is not sufficient. After exposure the loss of fluorescent intensity for these brightened fabrics is large, and sometimes yellowing is observed. As shown in Table 8, the fluorescent loss of these dyes on acrylic fiber on exposure is lower than that on the other substrates. Even by arc lamp irradiation for 20 hours, the fluorescent decay or yellowing of these dyes on acrylic fiber is not observed under daylight by visual assessment.

Table 8. Results of Lightfastness.

Dye No.	(Cashmilon F)					Dye No.	(Cashmilon F)				
	wave-length (m μ)	Relative intensity at exposure hours					wave-length (m μ)	Relative intensity at exposure hours			
		0	1	2	5			0	1	2	5
1	430	100	89	84	69	1'	430	100	96	90	82
2	430	100	86	77	52	2'	430	100	69	85	68
3	430	100	86	81	73	3'	430	100	97	88	79
4	430	100	92	81	72	4'	430	100	94	90	83
5	430	100	84	79	56	5'	430	100	95	85	73
6	430	100	90	83	80	6'	430	100	96	92	85
7	430	100	87	82	78	7'	430	100	89	85	81
8	430	100	91	85	77	8'	430	100	94	91	82
9	430	100	89	82	76	9'	430	100	95	92	83
10	430	100	90	80	75	10'	430	100	93	90	84
11	430	100	87	80	75	11'	430	100	93	90	85

Dye No.	(Vinylon)					Dye No.	(acetate)				
	wave-length (m μ)	Relative intensity at exposure hours					wave-length (m μ)	Relative intensity at exposure hours			
		0	1	2	5			0	1	2	5
1'	430	100	91	82	60	1'	430	100	85	82	66
2'	430	100	92	81	55	2'	430	100	85	82	67
3'	430	100	95	84	49	3'	430	100	86	76	46
4'	430	100	99	94	70	4'	430	100	92	88	69
5'	430	100	96	91	64	5'	430	100	98	94	75
6'	430	100	78	53	38	6'	430	100	78	62	40
7'	430	100	87	73	40	7'	430	100	69	53	34
8'	432	100	82	63	36	8'	430	100	87	71	47
9'	432	100	78	62	39	9'	430	100	74	61	35
10'	432	100	73	60	37	10'	430	100	68	53	34
11'	432	100	76	63	36	11'	430	100	76	63	36

N-substituted aminomethyl compounds generally show sufficient fastness, but dihydroxyamino and morpholino derivative (No. 3), (No. 5) and their quaternary salts (No. 3') (No. 5') do not show adequate lightfastness, while N-substituted sulfamoyl series have excellent lightfastness on acrylic fiber without exception.

From these data, it is concluded that the fluorescent brightening dyes containing cationic group, especially quaternary salt type dyes synthesized in this paper, with the few exceptions as mentioned above, show a remarkable brightening effect and an excellent fastness to light on polyacrylonitrile fiber.

Acknowledgment

The authors wish to express their gratitude to Daito Chem. Ind. Co. Ltd. for having offered the samples. The authors also wish to thank Mr. I. Araki for his assistances in this work.

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