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Synergism with Binary Mixtures of Fluorescent Whitening Agents

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ABSTRACT

The whiteness effects of 11 fluorescent whitening agents were compared with their binary mixtures in various mixture ratios. When they were simultaneously applied, a super-additive whiteness effect on polyester staple textile was found for most of them. The following observations were made: (a) two components in the mixture did not interfere with respect to the optical and dyeing behavior of each component; (b) the fluorescence quantum yield of a fluorescent whitening agent increased with decrease in concentration, within a certain range; (c) there was a difference of build-up rate between baths of low and high concentration. The latter two factors are probably responsible for the synergism effect noted with a binary mixture of fluorescent whitening agents.

1 INTRODUCTION

Synergism, i.e. the observable or measurable enhancement of the effect of a combination of substances compared with that of the same amount of individual components, is often encountered in textile treatments and finishings. Fluorescent whitening agents (FWAs) are organic compounds which can absorb below 400 nm and emit above 400 nm. Several reports[1] on the synergistic effects of FWAs, as well as of disperse dyes, have been made and numerous patent applications have been disclosed and commercial products developed, e.g. Hostalux EBU, Hostalux ENU-250 and Hostalux ETR (Farbwerke Hoechst AG). However, these patents give only the

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composition of the products with synergistic effects, and they do not give an explanation of the causes of the synergistic effects. This present paper is an attempt to elucidate the cause of the synergism observed during application.

2 EXPERIMENTAL

2.1 Materials

The 11 FWAs shown in Table 1 were used. The synthesis of these compounds has been previously reported.[2]

2.2 Instrumentation

Absorption and fluorescence spectra measurements were made using a Shimadzu UV-365 spectrophotometer and a Hitachi 850 fluorimeter, respectively. Fluorescence quantum yield values were determined by the relative method.[3] The fluorescent standard was quinine sulfate (0·01M) (fluorescence quantum yield value 0·55). The degree of whiteness measurements were made using an SBD-1 Whitemeter (China).

2.3 Whitening method

Individual FWAs or FWA mixtures in various ratios (100 mg) were dissolved in 5 ml concentrated sulfuric acid. The solution was quantitatively stirred into a solution containing 4 g dispersant, 6 g leveling agent, 300 g crushed ice and 490 ml distilled water, the pH adjusted with 10% NaOH to neutral and the volume made up to 1000 ml with distilled water.

The FWA dispersions were applied by the exhaust dyeing process, using pre-washed polyester staple fabric (100% PES). After applying at 130°C for 1 h the fabric was washed with water and dried at room temperature.

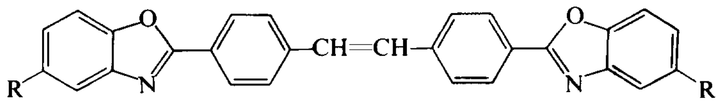
Prior to whiteness measurements, the whitened fabrics were stored at room temperature overnight.

3 RESULTS AND DISCUSSION

The maxima of the UV absorption and fluorescence emission spectra and their extinction coefficients, together with fluorescence quantum yields in DMF, are given in Table 2. The compounds absorbed between 350 and 385 nm and emitted between 430 and 452 nm, exhibiting high fluorescence quantum yields.

The results of the whiteness measurements both for single FWAs and their

TABLE 1
Structures of the FWAs

Number	*R*	*Molecular structure*
1	H	
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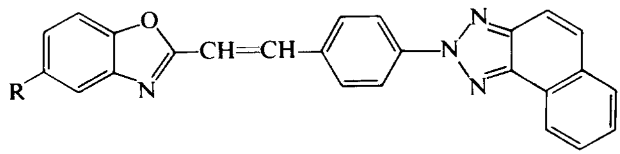
3	H	
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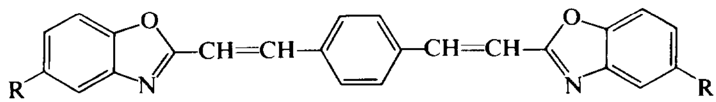
5	H	
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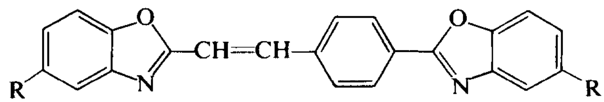
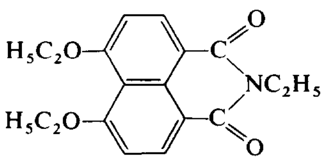
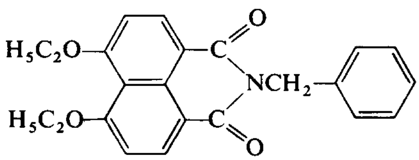
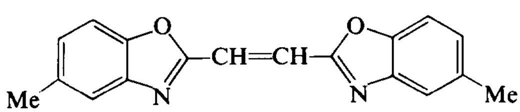
7	H	
8	Me	
9		
10		
11		

binary mixtures in various ratios are given in Table 3. Most of these show a synergistic effect but, in some cases, the effect is not apparent.

According to Martini & Probst,[4] three possibilities exist, as shown in Fig. 1, viz.:

(a) Whiteness effect is super-additive, within certain mixture ratios. The effectiveness of the mixture exceeds that of a single component, as shown in curve 3 (Fig. 1).

TABLE 2
UV Absorption and Fluorescence Emission Maxima, Extinction Coefficients and Fluorescence Quantum Yields in DMF

Number	λ^{a}_{max} (*nm*)	ε (*liter mol*$^{-1}$ *cm*$^{-1}$)	λ^{f}_{max} (*nm*)	ϕ (%)
1	354·0	76 200	433·7	79
2	376·0	77 300	435·7	89
3	368·8	66 800	431·0	84
4	373·6	69 400	431·9	86
5	382·0	70 600	447·4	86
6	384·0	78 400	452·4	87
7	362·4	52 700	429·7	86
8	377·0	54 000	435·2	88
9	364·0	12 300	436·5	89
10	381·4	18 500	440·0	80
11	362·5	43 000	425·5	78

(b) The whiteness effect of the mixture is super-additive, but below that of the individual value of the better component, as shown in curve 2.
(c) A purely additive behavior is obtained, as shown by the straight line 1.

However, no reason for the cause of the super-additive whiteness effect is given. On the basis of the results, however, the following explanations may be proposed.

(a) Two compounds in a mixture do not interfere with each other

Because the fixed state of an FWA on the fabric is predominantly in the single-molecular state,[5] the optical behavior of an FWA on the fabric may be considered to be analogous to its behavior in solution. The UV absorption spectra of compound **1**, compound **11** and their mixture is shown in Fig. 2. It is apparent that the spectrum of the mixture is a simple addition of the two components. This shows that the binary mixture is non-interactive with respect to light absorption. The data in Table 4 also confirm this.

The absorbance of the mixture may be expressed by

$$E_{m} = xE_{i} + yE_{j}$$

where E_m is the absorbance of the mixture, E_i and E_j are the absorbances of the two components, and x and y are the mixture ratios. The FL emission spectra of compound **1**, compound **11** and their mixture is shown in Fig. 3. This is similar to Fig. 2 and is non-interactive with respect to light emission.

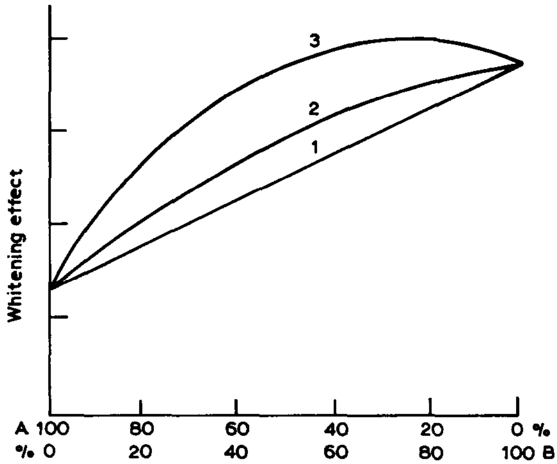


Fig. 1. Mixture dyeing curve of fluorescent whitening agents.

TABLE 3
Data on the Degree of Whiteness for Mixtures

Number	*Degree of whiteness*					
	0:100	*20:80*	*40:60*	*60:40*	*80:20*	*100:0*
1+2	95·6	104·7	105·9	105·1	102·1	91·9
1+3	96·8	105·5	106·0	105·2	101·4	91·9
1+4	98·4	99·4	100·9	102·0	101·0	91·9
1+5	113·7	114·0	114·1	112·7	109·8	91·9
1+7	92·3	98·5	102·8	103·5	102·4	91·9
1+8	95·9	100·2	100·6	99·1	97·2	91·9
1+9	89·7	96·7	102·5	104·1	102·0	91·9
1+10	98·2	99·6	100·7	102·7	100·3	91·9
1+11	90·6	96·2	100·2	102·5	102·7	91·9
2+4	98·4	99·6	101·5	101·1	98·6	95·6
2+6	113·9	114·9	113·1	112·9	104·5	95·6
2+7	92·3	99·0	101·5	102·1	100·2	95·6
2+8	95·9	99·2	103·5	104·8	104·5	95·6
2+9	89·7	98·5	102·0	103·0	102·4	95·6
2+10	98·2	98·3	98·5	99·7	98·9	95·6
2+11	90·6	100·9	101·7	102·1	102·5	95·6
3+4	98·4	99·1	101·2	102·7	100·0	96·8
3+7	92·3	100·1	102·7	105·2	106·2	96·8
4+8	95·9	99·5	102·0	100·2	99·2	98·4
7+8	95·9	99·1	100·7	97·7	94·6	92·3
7+11	90·6	95·2	98·2	97·6	95·9	92·3
8+11	90·6	97·5	98·7	99·7	99·5	95·9
9+11	90·6	94·8	94·6	94·4	93·5	89·7
10+11	90·6	97·4	98·0	98·1	98·2	98·2

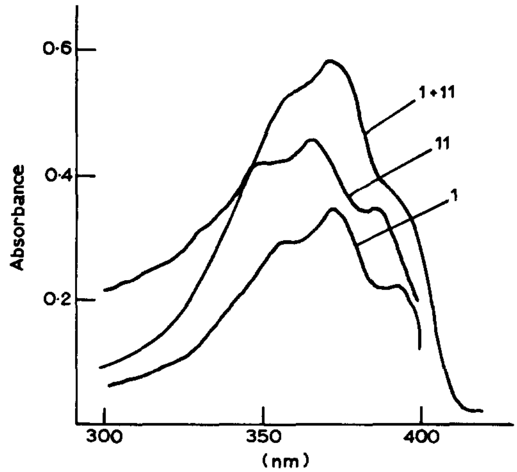


Fig. 2. UV absorption spectra of a mixture of compounds **1** + **11** and the two individual components in DMF.

It is apparent that the value of the fluorescence intensity is greater than that calculated using the relationship

$$F_m = xF_i + yF_j$$

(b) The fluorescence quantum yield of an FWA increases with decrease in the concentration of the solution, within a certain range

The whiteness effect of an FWA on the fabric is light-complementary and therefore the whiteness effect is relatable to the fluorescence intensity, which in turn is relatable to the concentration of the solution and to the fluorescence quantum yield on the fabric. On the one hand, the fluorescence

TABLE 4
Absorbance and Fluorescence Intensity of a Mixture of Compounds **1** + **11** and the Individual Components in DMF

Number	*UV (E)*	*FL* ($F \times 10^{-5}$)
1	0·044	1·482
11	0·055	1·413
1 + **11** (63:37)[a]	0·048	1·790
1	0·216	4·493
11	0·175	4·021
1 + **11** (50:50)[a]	0·193	4·443

[a] Mole ratio.

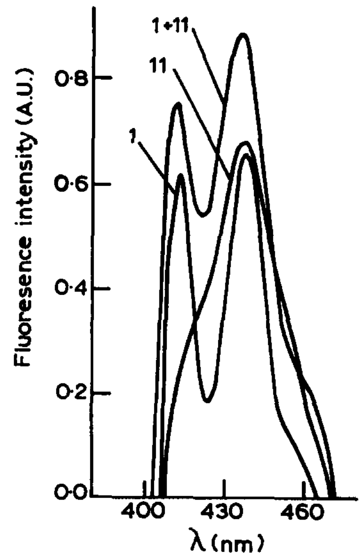


Fig. 3. Fluorescence spectra of the mixture of compounds **1**+**11** and of the two components in DMF.

quantum yield of an FWA (as shown in Table 5) increases with decrease in the concentration of the solution. On the other hand, the whiteness effect of an FWA on the fabric is appreciable only when the dyeing concentration of the FWA reaches a certain value. The whiteness effect is not appreciable below this critical value and a yellowing effect is observed above this value. When a mixed FWA is applied, the two individual components in the mixture decrease relatively in amount because they do not interfere with each other. This increases the fluorescence intensity and a super-additive whiteness effect is thus observed.

TABLE 5
Concentration Relationship Between Fluorescence Quantum Yield and Degree of Whiteness of Compound **11**

Dyeing concentration (%)	*FWA content* (*mg/160 ml*)	*FWA concentration* (M)	ϕ (%)	*Degree of whiteness*
0·01	0·2	4.3×10^{-6}	78	85·1
0·05	1·0	2.2×10^{-5}	72	87·4
0·10	2·0	4.3×10^{-5}	69	90·6
0·25	5·0	1.1×10^{-4}	64	92·3
0·50	10·0	2.2×10^{-4}	60	100·2
1·00	20·0	4.3×10^{-4}	55	Yellowing

(c) In the range of concentrations shown in Table 5, the build-up rate of an FWA by the fabric increases with decrease in dyeing strength

The fluorescence intensity emitted by an FWA on the fabric is also relatable to the amount of the FWA on the fabric, otherwise it cannot be explained why, as the dyebath concentration is higher and fluorescence quantum yield of the dyebath is lower, the whiteness effect is higher. The relationship between the build-up rate and dyeing concentration is the same as that for a disperse dye. A lower concentration in the dyebath shows a build-up rate higher than that of a higher concentration in the dyebath. When a mixed FWA is applied, the effective concentration of the two components both decrease relatively, and any one component is exhausted by the fabric at a higher build-up rate. Thus, the amount taken up by the fabric is super-additive.

The latter two factors existing simultaneously in the mixed dyebath and dyeing process result in enhancement of the amount of fluorescence intensity of two FWAs on the fabric, and therefore a synergism effect is observed during application.

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