

Effect of disperse red dye on spectral red-shift of green-emitting luminous fibre

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Green-emitting rare earth luminous fibre has been dyed with disperse red fluorescent dyestuff and ordinary disperse red dyestuff respectively, and the effects of disperse red dyestuffs on the spectral red-shift of green-emitting rare earth luminous fibre are studied by testing the luminescent properties. The emission spectra of green-emitting luminous fibre dyed with Red 3B, Red SE-GFL and Red S-2GFL show that the emission peak of fibre moves towards 620 nm from 520 nm after being dyed with Red 3B, and the spectrum has the strongest emission intensity when the concentration of Red 3B dye is 1.0% (o.w.f). The result of colorimetric analysis shows that the luminous fibre dyed with Red 3B dye at different concentrations has similar color purities, and the emission color of fibre is found closest to red color for the dyestuffs concentration of 1.0% (o.w.f). The analysis of energy transfer model of the dyed luminous fibre indicates that the light emitted by the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor could be used as a light source to excite the Red 3B dye, and the color of dyed luminous fibre is due to the blended luminescence color of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor and Red 3B dye.

Keywords: Fluorescent dye, Green-emitting fibre, Rare earth luminous fibre, Red-shift, Polyethylene terephthalate

1 Introduction

Rare earth luminous fibre is a new type of functional fibre, which can absorb sunlight in wavelength range 200-600nm and then release this light energy in the form of visible light. Usually this fibre can emit a strong fluorescence over 8 h in darkness or low light background even after the excitation light source is removed¹. This luminous fibre was prepared by adding the rare earth luminescent particles and nano-additives into the spinning polymer base materials such as polyester, nylon and polypropylene in the spinning process, and the luminescent particles in the fibre would serve as a light source. Now this fibre has been widely used in home textiles, clothing label, toy, decorations and anti-counterfeit technology²⁻⁴.

At present, the aluminate luminescent particle doped with the rare-earth ion of Sr and Dy, such as Sr^{2+} and Dy^{3+} doped strontium aluminate ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$) is the most common luminescent material used in luminous fibre because of its excellent performance of high brightness, long afterglow time, chemical stability and non-radiation⁵. However, the color of the fluorescence emitted by aluminate luminescent material of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ is monotonous with wavelength at around 520 nm, thus the luminous fibre can only show a green color in the dark, and its application performance is limited to some extent⁶. In order to increase the emitting color range

of luminous fibre, researchers have focused on preparing new kinds of long-lasting luminescence materials with different emitting color. After several years of efforts, luminous fibre with blue emitting color has been successfully prepared by adding the blue emitting long-lasting material $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ into the spinning solution⁷.

However, both the blue and green color belong to cool-toned color, which is also too monotonous to satisfy people's need for the warm-toned luminous fibre, especially for red-emitting luminous fibre. According to the chroma theory, any color could be obtained by adjusting the proportion of the three-primary colors, blue, green and red⁸. Therefore, for the red emitting luminous fibre with strong brightness and long luminescence duration, we can prepare luminous fibre with any emitting color we need.

As it is well known to all, the emitting color is mainly decided by the luminescence color of the long-lasting material which is contained in the fibre. As a consequence, preparing long-lasting phosphor having strong luminescence brightness and red emitting color has received the most interest in recent years, and hence several kinds of red emitting phosphor have been successfully prepared, such as $\text{Y}_2\text{O}_2\text{S}:\text{Sm}^{3+}, \text{Ti}^{4+}, \text{Mg}^{2+}$ reported by Li *et al.*⁹; $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Zn}^{2+}, \text{Ti}^{4+}$ prepared by Cui *et al.*¹⁰ and the $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ proposed by A.G. Ali *et al.*¹¹. However, all of these red-emitting luminescent materials cannot satisfy the application requirements of the luminous fibre because of the low intensity of

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luminescence, short decaying time and bad water resistance.

In order to investigate the possibility of preparing red-emitting luminous fibre by dyeing the green-emitting luminous fibre with disperse red dyestuff, in this study a red disperse fluorescent dye (Red 3B) and another two kinds of common red disperse dyestuffs (Red SE-GFL and Red S-2GFL) have been used to dye the green-emitting luminous fibre, and the influence of these dyestuffs on the color and emission spectra red-shift of green-emitting luminous fibre is investigated. Some significant conclusions have been obtained which would contribute to develop colorful luminous fibre with strong brightness and long duration time.

2 Materials and Methods

2.1 Materials

Rare earth luminous fibre (polyethylene terephthalate used as base material) was supplied by Changshu Jianghui Fibre Products Technology Co, Ltd, Suzhou, China. Disperse red dyestuffs (Red 3B, Red SE-GFL and Red S-2GFL), acetic acid and soft detergent were purchased from Sinopharm Chemical Reagent Co., Ltd China. The functional additives were supplied by Jiangsu Guoda Complete Wiring Equipment Co., Ltd, Wuxi, China. Molecular structure of disperse dyestuffs is shown in Structure 1.

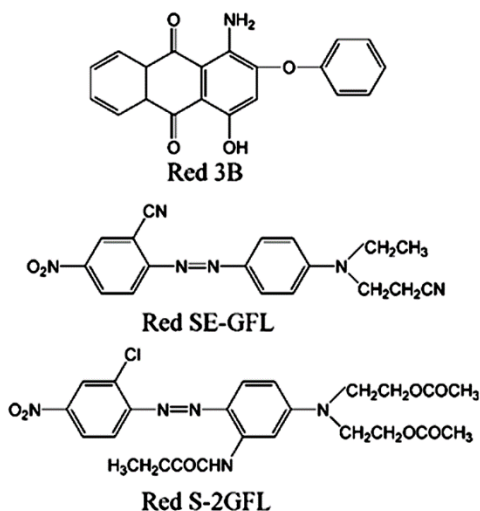
2.2 Dyeing Method

The dyeing process was carried out in stainless steel beaker bath having a temperature controller. The dye liquor of 2% (o.w.f) was composed of 50 mL of 0.1% of acetic acid and 0.2% uniform dyeing auxiliaries at a

bath ratio of 1:50. The dyeing system was maintained at pH 4-5. After the dye temperature was raised to 60 °C, the luminous fibres were cut into a length of 50cm and then 10 g of fibres was bounded together. The bounded fibres were then immersed into the dye bath, and the liquor temperature was raised to 130°C under a high pressure for 50 min and at a heating rate of 1°C / min. In this study, we set up two groups of trails to investigate the effects of red disperse dyestuffs on the color and emission spectra red-shift of rare earth luminous fibre. In the first group of experiment, the green-emitting rare earth luminous fibres were respectively dyed with Red 3B, Red SE-GFL and Red S-2GFL, and the concentration of dyestuff was 1.5% (o.w.f). In the second group, the green-emitting rare earth luminous fibres were dyed with Red 3B considering the dyestuffs concentration from 0.5% (o.w.f) to 2.0% (o.w.f) respectively. Finally, the dyed fibres were soaped at 70 °C with soft detergent. The dyeing procedure is shown in Fig. 1.

2.3 Characterization

The photoluminescence performances (excitation and emission spectrum) of the fibre were tested by a Hitachi F-4600 spectrophotometer equipped with a 150 W



Structure 1 — Molecular structure of dyestuffs

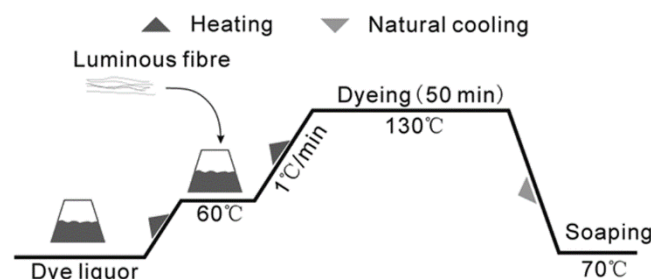


Fig. 1 — Dyeing procedure of luminous fibre

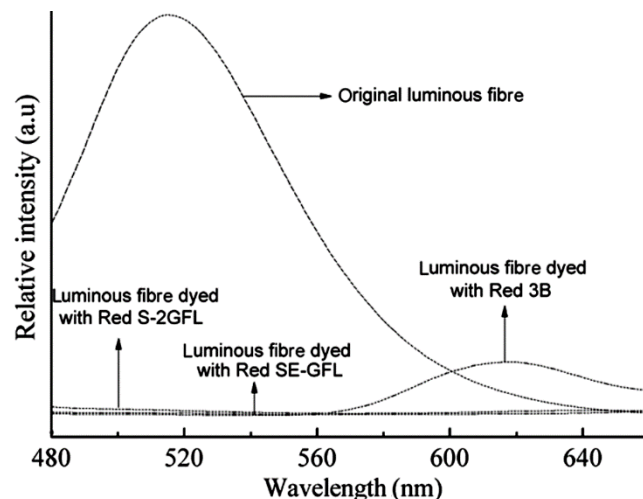


Fig. 2 — Emission spectra of luminous fibre samples

xenon lamp as the excitation source, the excitation wavelength ranged from 200nm to 800 nm and the scan speed was 120 nm/min. Chromaticity coordinates were measured and chromaticity diagrams were recorded by using a PR-650 spectra scan colorimeter (Photo Research Inc.).

3 Results and Discussion

3.1 Effect of Disperse Red Dyestuffs on Emission Spectra of Luminous Fibre

Figure 2 shows the green-emitting emission spectra of luminous fibre dyed with Red 3B, Red SE-GFL and Red S-2GFL respectively. It can be seen from Fig. 2 that the emission peak of green-emitting luminous fibre is at the wavelength of 520 nm, which corresponds to the characteristic emission peak of rare earth strontium aluminate phosphor. It means that fluorescence of the fibre is totally due to the rare earth strontium aluminate phosphor in the fibre. There is no emission peak of luminous fibre detected when the fibre is dyed with Red SE-GFL and Red S-2GFL. However, the emission peak of fibre is moved towards the wavelength of 620 nm from 520 nm (spectral red-shift) after the luminous fibre is dyed with Red 3B.

It is well known that the phosphors are added into the spinning solution during the spinning process and would be uniformly distributed in the fibre with the help of a special dispersant. Thus, the phosphors included in the fibre are the fluorescence source of the luminous fibre in the dark. When the fibre is exposed to the sun, the light reaches on the surface of the fibre, except that a little amount of light is reflected to the air, most of the light penetrates the fibre and transfer to the surface of the phosphors. Then the light energy would be absorbed by the phosphors included in the luminous fibre and this energy would be converted into light, which is continuously released by the fibre. As indicated in Fig. 2, the emission peak of green-emitting luminous fibre at an wavelength of 520 nm is corresponded to the typical transmission energy levels of Eu^{2+} ion from $4f^65d^1$ to $4f^7$ (refs 12, 13). For the dyed luminous fibre, the dyestuffs enter into the amorphous region of the luminous fibre and then are attached to the surface of the phosphors that disperse in luminous fibre. Therefore, the light released by phosphors would be absorbed or reflected by the dyestuffs. It is observed that the emission spectra of the luminous fibre turn an apparent red shift after being dyed with the anthraquinone structure of Red 3B, which may be attributed to the fluorescence groups contained in its molecular structure. However, for azo dyestuffs of Red

SE-GFL and Red S-2GFL, their structure contains electron-withdrawing groups, which would hinder the shell electrons transferring between excited states and ground state and leading to the die out of fluorescence.

3.2 Effect of Red 3B Concentration on Spectra of Luminous Fibre

In order to investigate the effects of different concentrations of the Red 3B dyestuff on the luminous fibre luminescent property, the excitation and emission spectra of the luminous fibre are measured. The excitation peak of the original luminous fibre is observed at wavelength 365 nm, corresponding to the peak of phosphors excitation spectra, which is mainly caused by 5d electron transition of the rare earth ion Eu^{2+} between different energy levels¹⁴. As can be seen in Fig. 3(a), the excitation spectrum of the fibre moves towards the longer wavelength direction (red-shift) after being dyed with Red 3B dyestuff as compared to the original fibre. However, the intensity of the excitation spectrum increases dramatically at first and then decreases when the doping ratio of dyestuffs is over 1.0% (o.w.f). The emission spectra of the dyed

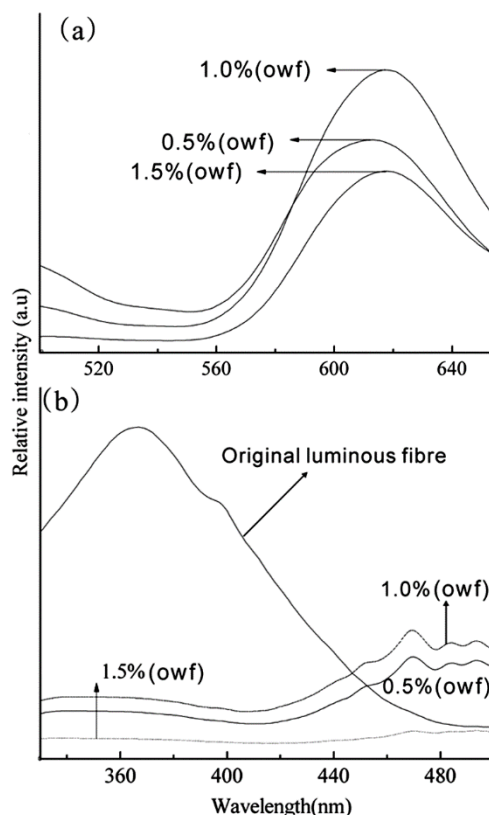


Fig. 3 — Excitation spectra (a) and emission spectra (b) of the luminous fibre after being dyed with different dyestuffs concentration

luminous fibre are shown in Fig. 3(b). It is vivid that the varying trend of emission spectrum has the same changing tendency with the excitation spectrum after the original luminous fibre is dyed with Red 3B dye, and when the dye concentration of Red 3B is 1.0% (o.w.f), the emission spectrum of dyed luminous fibre has the strongest emission intensity at wavelength of 620 nm. The reason may be ascribed to the covering effect of Red 3B dyestuff. When the concentration of dyestuff is less than 1.0%, the amount of dye that enters into the luminous fibre is not enough to completely cover the phosphors, and hence the phosphors, included in luminous fibre, could still obtain a lot of energy from the exciting light source, and then emit a green light which would transfer towards the dyestuff to excite it. At a certain concentration range, the more dyestuff entered into the luminous fibre, the more the dyestuff would be excited by the green light emitted by the phosphors, leading higher luminescent intensity. So, excitation spectrum and emission spectrum intensity of the luminous fibre dyed with 1.0% of Red 3B is stronger than the luminous fibre dyed with 0.5% Red 3B. However, with the increasing concentration of dye, more and more phosphors included in the fibre are completely covered by the dyestuff, and hence the light energy is not sufficiently absorbed by the phosphor. As a consequence, the luminescence released by the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor decreased gradually, and the dye on the surface of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor also cannot be excited completely. Hence, the intensity of the excitation and emission spectra of the dyed luminous fibre declines rapidly when the concentration of the dye is raised to 1.5% (o.w.f).

3.3 Colorimetric Analysis

Based on what has been discussed above, it can be concluded that the Red 3B dye has a certain impact on the emission spectra of the luminous fibre. According to the emission spectra of the dyed luminous fibre, the chromaticity parameters are calculated in Table 1. Based

Table 1 — CIE1931 chromaticity coordinates and color parameters of the luminous fibre after being dyed with different concentrations of Red 3B dye

Dyestuffs concentration, % (o.w.f)	Chromaticity coordinates		Color purity, %
	x	y	
0	0.2762	0.5774	58
0.5	0.5210	0.4135	89
1.0	0.5951	0.3865	94
1.5	0.6094	0.3726	95

on the x and y values of chromaticity coordinates, the CIE 1931 chromaticity coordinate diagram of rare earth luminous fibre is obtained, (Fig. 4). It can be seen that the color of the original luminous fibre is located in the green area, while the color of the luminous fibre dyed with Red 3B is primarily located in the orange-red area, and it continues to move towards red area with the increase of the dye concentration. In addition, the color purity of the dyed luminous fibre increases significantly compared with the original luminous fibre, and it rises to 94% when the concentration of the Red 3B dye is 1.0% (o.w.f).

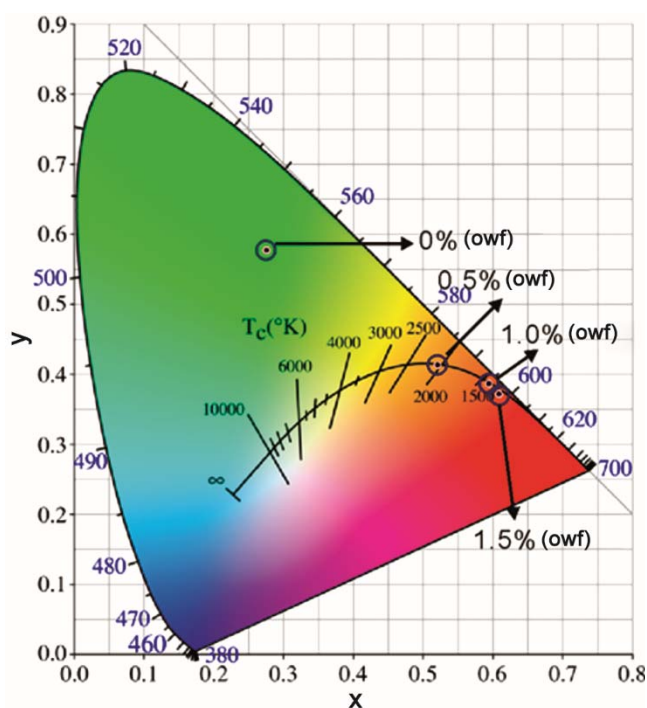


Fig. 4 — CIE 1931 chromaticity coordinate diagram for samples

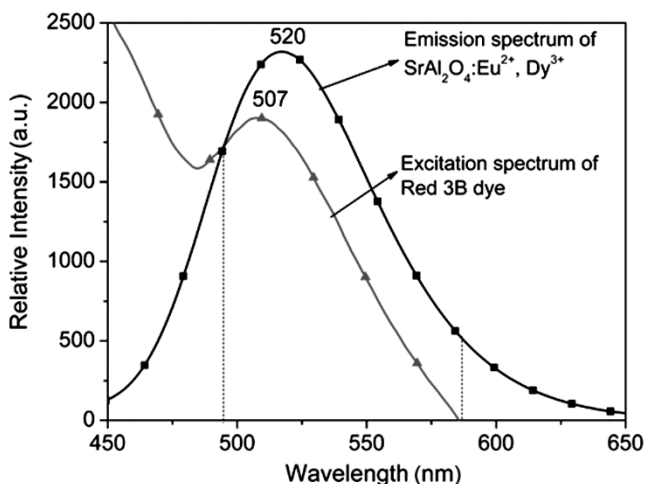


Fig. 5 — Excitation spectrum of Red 3B dye and emission spectrum of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor

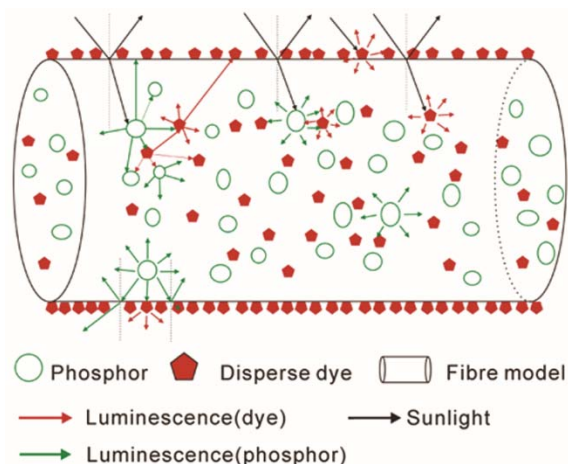


Fig. 6 — Energy transfer model of dyed luminous fibre

However, the value of color purity increases slowly after the concentration of Red 3B dye exceeds 1.0% (o.w.f), which is similar to the changing trend of emission color.

3.4 Energy Transfer Model of Dyed Luminous Fibre

In order to clarify the reason of spectral red-shift of the dyed luminous fibre, the excitation spectrum of the dyestuffs (Red 3B) and the emission spectrum of the phosphor ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$) are measured (Fig. 5). Apparently, there is an overlapped area between the emission spectrum of the phosphor (black line) and the excitation spectrum of the Red 3B dye (red line) in the wavelength range of 495-587 nm. Besides, it can be seen that the excitation peak of the Red 3B dye (507 nm) is close to the emission peak of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor (520 nm). According to the theory proposed by the Dexter that, the energy transferring between two kinds of substances could happen if there is an overlapped area between the emission spectrum of the sensitizing ions and the excitation spectrum of the active ions, which means that the luminescence emitted by the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor could be used as a light source to excite the dyestuff.

Figure 6 shows the energy transfer model of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor and the Red 3B. After the original luminous fibre is dyed with Red 3B, most of the dye would cling to the surface of the fibre, and part of the dye would infiltrate into the fibre. When the fibre is exposed to sunlight, the light reaches to the surface of the fibre, and then it would mainly divided into three parts, namely the first part would be reflected back to the air, the second part would be absorbed by dye on the surface of the fibre, and the last part of light would enter into the fibre and absorbed by the internal dyestuffs and phosphors. In a dark condition, the internal phosphor

would emit its characteristic light. Part of the fluorescence light penetrates the fibre and then pass into the air again, another part of fluorescence light would deliver to the dye and serve as the excitation resource, and then the red dyestuff would emit its characteristic light, so the color of total luminous fibre observed by eyes is a blended effect of two kinds of lights from the phosphor and the disperse red dye.

4 Conclusion

4.1 The emission spectra of the luminous fibre has apparent red-shift after being dyed with Red 3B dye where the peak of the spectrum moves towards 620 nm from 520 nm, and the spectra has the strongest emission intensity when the fluorescent Red 3B concentration is 1.0% (o.w.f). However, the emission intensity of luminous fibre decreases after dyeing.

4.2 The luminous fibre dyed with fluorescent Red 3B dye in different concentrations has similar color purities, and the emission color of fibre is found closest to the red color when the concentration is 1.0% (o.w.f).

4.3 There is an energy transfer in the luminous fibre after being dyed with fluorescent Red 3B dye, and the color of the dyed luminous fibre consists of the blended luminescence color of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor and Red 3B dye.

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