Scientific Research

Study on Fluorescence Intensity Determination of Rare Earth Europium Complexes UV-Photochromic Inks

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Abstract: The paper discussed the preparation of rare earth europium complexes ultraviolet rays (UV) photochromic ink and the influences of factors, such as europium complexes using a rare earth ternary complex of Eu ion with 3-benzoylbenzoic acid and phenathrolinephen [$Eu(BA)_3Phen$] content upon printing ink formula. In the experiment, we utilized fluorescence spectrophotometer to make quantitative determinations of the relative fluorescence intensity of rare earth europium complexes and different proportions of UV photochromic ink samples. Besides, we made further analysis and studied their relative fluorescence intensity and fluorescence spectrum. Printing ink samples were made in the offset printability tester with the pressure of 200N, 500N, or 800N.The results showed that: printing pressure had a little influence on the fluorescence intensity of samples, for instance, with the 500N pressure, the relative fluorescence intensity could be easily tested; with rare earth europium complexes proportion increasing, the relative fluorescence intensity became enhanced. In this paper, we studied the relative fluorescence intensity for different proportions of photochromic ink. It demonstrated that through the quantitative determination of the relative fluorescence intensity of samples, the best content ranges for adding rare earth europium complexes was between 8.5% and 9.5%. From the fluorescence spectrum, we got conclusion that photochromic ink reached the crest of 616.8nm.

Keywords: rare earth europium complexes; dispersed system; granularity; the relative fluorescence intensity

1. Introduction

In recent years, photochromic materials research has been constantly developed, and people pay more and more attention to the rare-earth ions in fluorescent performance. At present, rare earth europium complexes has been applied in China, and prepared UV-curing of rare red fluorescent security inks [1]. We prepared rare earth europium complexes UV-photochromic inks. Under UV radiation, $Eu(BA)_3Phen$ can show red fluorescence, and have excellent performance on the absorption of UV and reflection of red fluorescence. Through the quantitative measurements of the relative fluorescence intensity of photochromic ink, illumination performance was better researched, and played a significant role on quantification analysis.

2. Preparation of $Eu(BA)_3Phen$ dispersed system and photochromic ink

According to GB/T 17001.1-1997, anti-forgery ink part 1: technical conditions of UV fluorescence excitation ink (hectograph, typography), requiring the granularity of photochromic materials of $Eu(BA)_3Phen$ to be less than 15μm[2], then refining $Eu(BA)_3Phen$ to solve the cohesion problem when joined in the ink, and get photochromic ink.

2.1 Experiments

Instruments:

D8401 ZH - an electric mixer, Laser particle size analyzer S3500 (origin: USA), Outsourcing glass beads (diameter 6mm), 50ml beaker, AB2042S electronic analytical balance.

Materials:

soybean oil, $Eu(BA)_3Phen$, sodium polyacrylate, white light quick-drying offset printing ink (Outsourcing).

Methods :

(1) the scattered distribution system: compounding europium- benzoic acid- phenanthroline and soybean oil (mass ratio of 1:1) in the beaker, then adding 2‰ dispersant of sodium polyacrylate and a few glass beads, stirring 24 hours, we got lanthanide europium complexes dispersion and measured the particle size distribution.

(2)Rare earth europium complexes UV-photochromic ink: put amount of dispersion into white offset printing ink and stir the fluid, then produce the UV-photochromic ink, the share of $Eu(BA)_3Phen$ are 2%, 4%, 6%, 8%, 10%, 12%, 14%, 16% respectively.

2.2 The measurement of the particle distribution of $Eu(BA)_3Phen$ dispersed system

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The national standard was achieved and the cohesion problem when mixing with ink was made out by $Eu(BA)_3Phen$. Determination of particle size distribution as follows: take a little of dispersion and diluted with proper ethyl acetate. The curve of size distribution, which determined by the laser particle size analyzer S3500, was shown in fig.1.

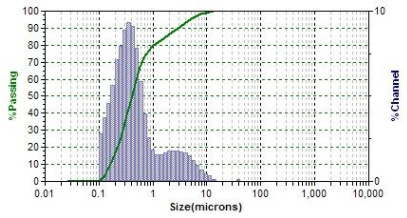

Figure 1. Size distribution curve of lanthanide europium complexes dispersion

Table 1. Size distribution of dispersion

Dia	Vol %	Width
0.4090	100.00	1.3930

Annotate: Dia shows grain size of the peak, the percentage composition within the scope of width is Vol%

As seen from fig.1 and tab.1, the particle size almost distributed within 10μm in only one area uniformly, and satisfied the standards.

3. Determination of the relative fluorescence intensity

The relative fluorescence was measured by fluorescence spectrophotometer quantitative measure method, which can show photoluminescence property more specific and directly. The excitation wavelength and emission wavelength of the $Eu(BA)_3Phen$ must be determined first, because they were the basic data for quantitative determination of relative fluorescence intensity.

3.1 Instruments and materials

Fluorescence spectrophotometer RF-5301 was purchased from Dao Jin Company, IGT2C1 offset printing was made in Holland, coated paper 80g/m^2, paper size was 45mm in width and 270mm in length.

3.2 Experimental methods

3.2.1 Confirmation of the excitation wavelength and the emission wavelength of $Eu(BA)_3Phen$ [3~6]

(1) Confirmation of the excitation wavelength of $Eu(BA)_3Phen$

Wavelength 334nm was basic excitation wavelength to detect the emission wavelength of $Eu(BA)_3Phen$. The emission wavelength was found at spectrum peak 616nm, which was the only maximum spectrum peaks.

Fluorescence emission wavelength parameter was set to 616nm, the scanning range was 220 to400nm, and its excitation wavelength was gained at 350nm.

(2) Confirmation of the best emission wavelength

Emission wavelength was adjusted by excitation wavelength 350nm. The instruments parameter was set as follows: excitation wavelength was 350nm, the scanning range was 500 to 700nm, low sensitivity, maximum spectrum peaks was 616.8 nm, namely the best emission wavelength was selected at 616.8 nm.

3.2.2 Selection of printing pressure

The samples were printed using photochromic ink, the printing pressure were 200N，500N, and 800N. Excitation and emission wavelength were 350nm and 616.8nm. The slit was EX: 5.0nm and EM: 1.5nm. The results were shown in tab. 2.

Table 2. Relative fluorescence intensity of samples under different printing pressure

Mass fraction(%)	Printing pressure(N)	Relative fluorescence intensity				
		1	2	3	4	5
4	200	64.937	70.89	71.417	66.442	69.539
	500	71.646	68.416	67.302	68.288	71.688
	800	73.828	77.091	81.606	73.047	70.281
6	200	94.397	98.359	104.217	98.269	98.088
	500	110.259	105.029	108.77	107.942	104.478
	800	108.651	108.089	108.906	115.67	110.119

As seen from Tab.2, the printing pressure had unobvious influence on the relative fluorescence intensity of photochromic ink, so the printing pressure was defined at 500N, and the effect of printing was better.

3.3 Results and Discussion

3.3.1 Selection of samples proportion [6~10]

The relative fluorescence intensity of samples with different contents of $Eu(BA)_3Phen$ were measured, data were given in tab.

Table 3. Relative fluorescence intensity of samples with different proportions

Mass fraction(%)	Relative fluorescence intensity					
	1	2	3	4	5	Average
4	101.283	103.888	104.229	96.648	101.572	101.524

6	129.049	130.647	133.182	123.306	113.746	125.986
8	158.759	164.074	166.482	166.447	163.089	163.7702
10	180.381	185.647	192.984	181.745	185.000	185.1514
12	254.692	272.933	266.62	243.128	268.563	261.1872
14	316.467	311.813	308.314	304.578	314.094	311.0532
16	356.545	350.398	358.643	349.532	364.718	355.9672

As seen from Tab.3, the increasing tendency of the relative fluorescence intensity became weaker obviously, when $Eu(BA)_3Phen$ mass fraction was between 8% and 10%. But considering minimizing the photochromic material quantities and controlling costs, best ratio of $Eu(BA)_3Phen$ and white offset printing ink should be found. Several smaller interval points were identified in the quality score of 7% to 10%, they were 7%, 7.5%, 8%, 8.5%, 9%, 9.5% and 10%. Then relative fluorescence intensity was tested following the process above.

3.3.2 Confirmation the optimum ratios of $Eu(BA)_3Phen$ and UV-photochromic ink

According to the same measure method, the relative fluorescence intensity of samples with different contents of $Eu(BA)_3Phen$ were tested, data were given in tab.4.

Table 4. Relative fluorescence intensity of samples with different proportions

Mass fraction (%)	Relative fluorescence intensity					
	1	2	3	4	5	Average
7.0	125.984	127.106	129.976	127.926	130.051	128.2086
7.5	130.775	132.206	133.229	140.321	138.914	135.089
8.0	146.093	147.696	151.588	152.677	156.309	150.8726
8.5	169.829	165.766	168.704	171.153	172.011	169.4926
9.0	167.142	166.445	170.361	170.923	171.439	169.262
9.5	172.355	178.095	177.342	177.034	180.992	177.1636
10.0	190.368	196.83	198.416	199.672	193.816	195.8204

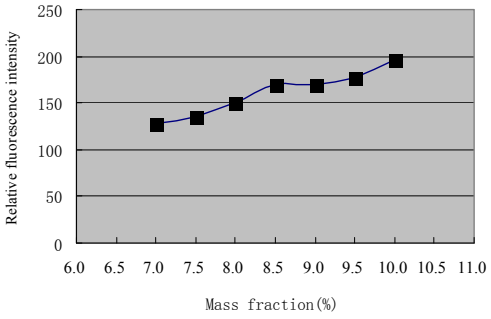

Figure 2. Relative fluorescence intensity of photochromic inks for different ratio

As seen from Figure 2, curve tendency generally rose, but in the same gap, the increase degree was different, in 8.5%, the increasing tendency of the relative fluorescence intensity became weaker suddenly. In interval 8.5 ~ 9.5%, increasing tend of relative fluorescence intensity became smooth with the increase of $Eu(BA)_3Phen$ content, relative fluorescence intensity of photochromic ink didn't increase obviously with $Eu(BA)_3Phen$ content. Considering to reduce costs and make good use of photoluminescence, the optimal ratio range was 8.5 ~ 9.5%, $Eu(BA)_3Phen$ UV- photochromic ink could demonstrate excellent photoluminescence properties.

4. Conclusions

(1)Experiments proved that relative fluorescence intensity of samples had a little influence on printing pressure, and the better printing pressure was 500N.

(2)The results showed that the optimal ratio range of $Eu(BA)_3Phen$ content was 8.5 ~ 9.5%.

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