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Determination of fluorescent whitening agent in emulsion paint based on fluorescence spectrophotometry

Lin Zhang*[1], Youlin Zhao[2]

[1]College of Science, Hohai University, Nanjing, P. R. China, 211100, hhuzhangl@126.com

[2]Business school , Hohai University, Nanjing, P. R. China, 211100, sobzyl@hhu.edu.cn

Abstract: Fluorescence spectrophotometry was applied to the determination of fluorescent whitening agent in emulsion paint. At temperature of 30℃, linear relationship was found between fluorescence intensity and concentration of fluorescent whitening agent in the range of 0.025-0.25mg/ml when the emission wavelength was 437nm and excitation wavelength was 347nm, correlation conefficient was 0.998, detection limit was 0.0007mg/ml, relative standard deviation ranged from 0.49% to 0.72%, recovery of standard addition ranged from 98.3% to 104.5%. The influence of storage time and exposure time were also studied here. Measurement results indicated the feasibility and precision of using this method for quantitative analysis of fluorescent whitening agent.

Key words: fluorescent whitening agent; emulsion paint; fluorescence intensity

1. Introduction

Fluorescent whitening agent (FWA) is an important functional auxiliary. The whitening mechanism of FWA can be described as follows: The FWA absorb ultraviolet light (340nm-380nm) which has the same characteristic frequency then emit visible light in the region of blue purple light (410nm-460nm). The white light can be obtained based on the complementary relationship between the emission ray and faint yellow light in the base material. So the whitening effect can be achieved[1]-[2]. So far, there are about 2500 kinds of FWA which belongs to 15 basic types. FWA is widely used in the textile, paper, plastics, paint and other industries[3].

Emulsion paint (EP) is a new type of decoration materials. Many transparent or white paint has an inherent yellow hue. Therefore, FWA has been widely used in the white and undertint EP. Based on the mixed light of blue purple light and white light, FWA can seem to be lily and brightsome[4]. Household interior-wall EP must be water-soluble and have a good compatibility with the other components. At the same time, the component ratio between FWA and EP must be suitable in order to obtain good whitening effect[5]. If the content of FWA in EP is overproof, the whitening effect can be

destroyed. When FWA gets on the skin, there will be an impact on the health[6]. Therefore, it's of great significance to provide impartial, accurate and fast measurement of FWA in EP.

Currently, the quantitative analysis methods for FWA consist of whiteness method[7], thin layer chromatography method[8]-[9], capillary electrophoresis method[10], high efficiency liquid chromatography method[11]-[12], ultraviolet spectrophotometry[13]-[14], fluorescence spectrophotometry[15]-[16]. The range of applications includes paper, water, detergent, textile, food and so on. But there is no reports about the measurement method of FWA in EP.

Based on fluorescence spectrophotometry, FWA content in EP is measured in this paper. According to the optical properties of the FWA, the best measuring wavelengh and temperature is selected. The standard curve can be obtained through the fluorescence spectrum measurement of the FWA-EP mixture. The percent recovery experiment is carried on here to verify the measurement accuracy of this method. Meanwhile, the influences of storage time and exposure time on the measurement results are also studied in this paper. Measurement results show that the method of fluorescence spectrophotometry can effectively realize the quantitative analysis of FWA in EP with high accuracy and credibility.

2. Experiment

2.1 Instruments and samples

All the fluorescence spectra were performed on a RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a 150-W Xenon lamp, using a quartz cell of 1.0 cm path length. All the absorption spectra were performed on a UV-3600 UV-VIS spectrophotometer (Shimadzu, Japan).

The Chinese name of the FWA studied in this paper is 4BK and the foreign name is Tinopal 5BM which belongs to the kind of acid double triazine FWA (anionic). The appearance is light yellow powder. The acid resistance is PH=2. The basic structure of 4BK is shown in figure 1.

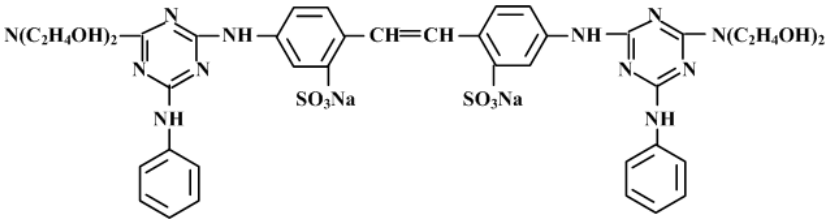

Figure 1. Chemical formula of FWA 4BK

The EP used in the experiment is household water dilution interior-wall coating. The ingredients consist of Palm oil, white latex, 107 glue powder, talcum powder, waterproof, ash calcium powder, light calcium carbonate, benzoic acid, sodium carbonate and ethylene glycol, tributyl phosphate and deodorant.

The water used in the experiment is sub boiling water. Analytical balance precision is 0.0001g, constant temperature water bath precision is 0.1℃, two kinds of brown conical flasks capacity are 250ml and 50ml, respectively, pipette capacity is 1ml.

2.2 Experiment method

Accurately weigh 0.1 g FWA 4BK and set the sample in the brown conical flask (250 ml). Then add sub boiling water to keep the capacity 200ml. This solution is the standard liquid of FWA with concentration of 0.5 mg/ml.

Accurately weigh 1ml, 2ml, 3ml.....10ml standard liquid in turn and set these sampes in ten brown conical flask (25ml). Then add EP to keep the capacity 20ml. The FWA concentrations of these calibration samples are 0.025mg/ml, 0.05mg/ml, 0.075mg/ml, 0.1mg/ml, 0.125mg/ml, 0.15mg/ml, 0.175mg/ml, 0.2mg/ml, 0.225mg/ml, 0.25mg/ml.

Before measurement, the temperature is set at 30℃ through the water bath. Add 3ml FWA standard sample into the cuvette with pipette. Absorption spectrum can be obtained with the UV3600 spectrophotometer with scanning range from 220nm to 400 nm. Fluorescence spectrum can be obtained with RF5301 fluorescence spectrophotometer with scanning range from 370nm to 560nm. The slit width is 1.5nm. Record the fluorescence intensity of the sampleS. The whole operation process is carried on in a dark room.

3. Results and discussions

3.1 Selection of the measuring wavelength

The UV3600 spectrophotometer is used to scan the absorption spectrum of the FWA standard liquid. The RF5301 fluorescence spectrophotometer is used to scan the fluorescence spectrum and excitation spectrum. Measuring results are shown in figure 2.

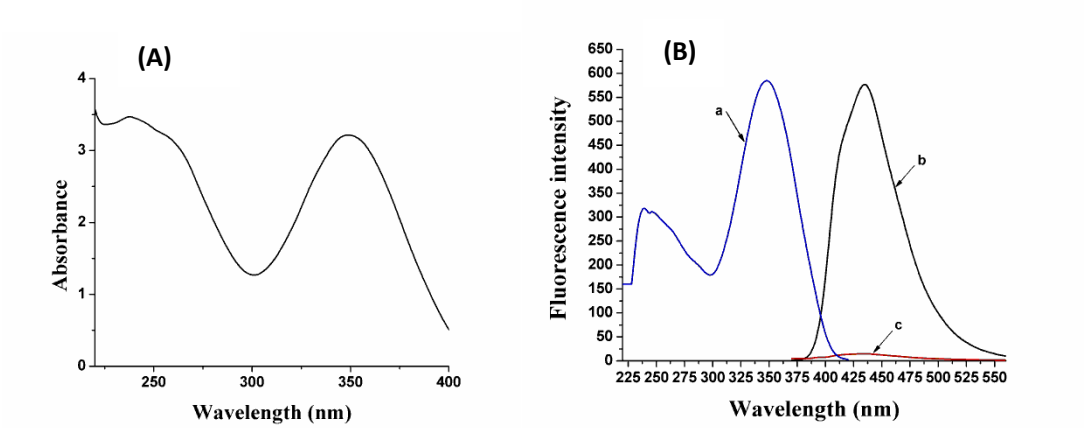

Figure 2. Absorption spectrum and fluorescence spectrum of the FWA standard liquid ((A)-absorption spectrum, (B): a-excitation spectrum of the FWA standard liquid, b- fluorescence spectrum of the FWA standard liquid, c-fluorescence spectrum of the EP)

It can be seen from the figure (A) that the strongest absorption peak of FWA standard liquid is at 347nm. It can be seen from the figure (B) that when the excitation wavelength is 347nm, there is an obvious fluorescence peak of FWA at 437nm while there is no fluorescence peak of EP here. According to the figure B(b), when the emission wavelength is at 437nm, the strongest excitation wavelength is 347nm. This result is in accordance with the results of absorption spectrum. Based on this results, the selected excitation wavelength is $\lambda_{ex} = 347nm$, the emission wavelength is $\lambda_{em} = 437nm$.

3.2 Selection of the measuring temperature

The fluorescence intensity of the FWA standard liquid is measured at the temperature of 20℃, 25℃, 30℃, 35℃, 40℃, 45℃, 50℃ and 55℃ when the excitation wavelength is 347nm. The whole operation process is carried on in a dark room. The results is shown in figure 3.

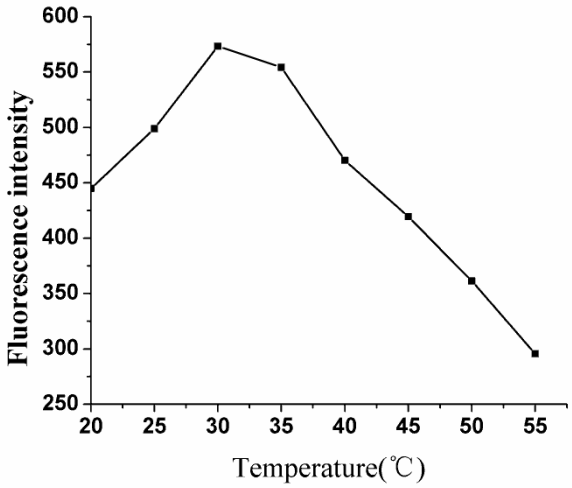

Figure 3. The fluorescence intensity of the FWA standard liquid at different temperatures

It can be seen from the figure that along with the increase of temperature, the fluorescence intensity of the FWA standard liquid at 437 nm increases first and then decreases, and reached the maximum at 30℃. Therefore, 30℃ is selected as the optimum measuring temperature.

3.3 Establishment of standard curve

The fluorescence spectrum of 10 samples is measured at 30℃ when the excitation wavelength is 347nm. The whole operation process is carried on in a dark room. The results is shown in figure 4.

It can be seen from the figure that along with the increase of the concentration of FWA, the fluorescence intensity will also increases. The fluorescence intensity of the mixture of FWA-EP at 437nm (take off the fluorescence intensity of EP at 437nm) and the concentration of FWA are used to obtain the linear standard equation. The fitting equation is Y=1000X+12, where X is the concentration of FWA (mg/ml) and Y is the fluorescence intensity of the sample (take off the fluorescence intensity of EP). The correlation coefficent is 0.998.

According to the research results in reference [17], when the ratio of the FWA and EP is 0.02%, the whitening effect is optimal. Based on the this optimal ratio, when the concentration of FWA is not more than 0.2mg/ml, we can get the best whitening effect. So, according to the measurement results, when the concentration of FWA ranges from 0.025mg/ml to 0.25mg/ml, there is a good linear relationship between the concentration and fluorescence intensity.

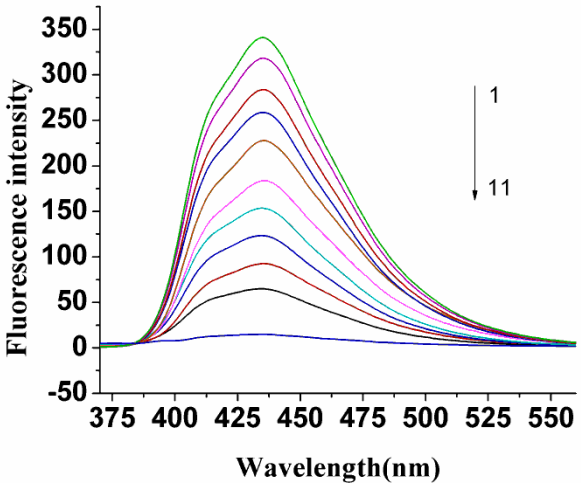

Figure 4. Fluorescence spectrum of FWA-EP (Top to bottom, 1-10: mixture of FWA-EP, the concentration of FWA is 0.25mg/ml，0.225mg/ml，0.2mg/ml，0.175mg/ml，0.15mg/ml，0.125mg/ml，0.1mg/ml，0.075mg/ml，0.05mg/ml，0.025mg/ml, respectively, 11: EP).

3.4 Percent recovery experiment

Accurately weigh 1.5ml, 2.5ml, 3.5ml, 4.5ml, 5.5ml, 6.5ml, 7.5ml, 8.5ml, 9.5ml standard liquid in turn and set these sampes in ten brown conical flask (25ml). Then add EP to keep the capacity 20ml. The fluorescence intensity of the samples at 437nm are measured at the temperature of 30℃. According to the standard equation, the concentration of FWA can be calculated. The percent recovery (R%) and relative standard deviation (RSD) can also be obtained at the number of measurements n=4. The whole operation process is carried on in a dark room. The results is shown in table 1.

Table 1 Results of percent recovery experiment

Standard value (mg/ml)	Average measurement value (mg/ml)	RSD (n=5)	R%
0.0375	0.0392	0.49%	104.5%
0.0625	0.0643	0.52%	102.9%
0.0875	0.0889	0.64%	101.6%
0.1125	0.1106	0.69%	98.3%
0.1375	0.1362	0.72%	99.1%
0.1625	0.1609	0.59%	99%
0.1875	0.1902	0.63%	101.4%
0.2125	0.2141	0.62%	100.7%
0.2375	0.2365	0.71%	99.6%

It can be seen from the table that RSD ranges from 0.49% to 0.72% and the percent recovery ranges from 98.3% to 104.5%. This shows that the method is good at the precision and repeatability. The measurement error at high concentration is bigger than that at low concentration.

3.5 Measurement of detection limit

According to the fluorescence intensity of blank reagent (EP without FWA) at 437nm (Measurement of 24 times), the average measurement value is X_B=11.865 and standard deviation

S_B=0.226. Based on the ratio of three times of standard deviation and slope of the standard equation, we can calculate the detection limit of this method is 0.0007mg/ml.

3.6 Stability of the standard sample

The standard liquid of FWA is set in the refrigerator lucifugally. The fluorescence intensity at 437nm is measured for ten consecutive days. Befoure measurement, the temperatures of the samples are kept at 30℃ with water-bath. The results are shown in figure 5.

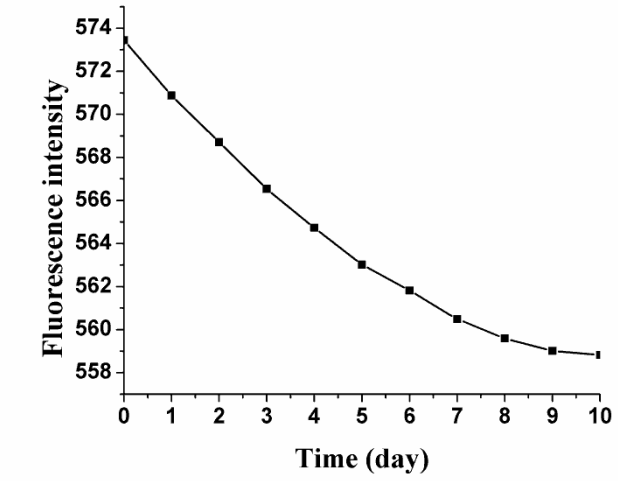

Figure 5. Stability of the standard liquid of FWA

It can be seen from the figure that fluorescence intensity reduces by 14.634 on the tenth day. According to the standard equation, the measurement results can be influenced by 0.003mg/ml. So, when the sample is configured, the measurement should carry on the same day to avoid influence on the result of measurement.

3.7 Influence of exposure time

Standard liquid of FWA is studied in the following three exposure environment: (1) Outdoor sunlight exposure; (2) UV lamp with the center wavelength of 365nm and 0.1mw power; (3) Common daylight lamp. After exposure, the temperature of the sample is kept at 30℃. The fluorescence intensity at 437nm is measured. The results are shown in figure 6.

It can be seen from the figure that when the FWA solution is set under the outdoor sunlight, the fluorescence intensity decreases with exposure time rapidly. When the exposure time is more than 80s, the fluorescent intensity is basically stable; When the FWA solution is set under UV lamp, the fluorescence intensity decreases with the exposure time. But the variation rate is lower than that in the sunlight. When the exposure time is more than 100s, the fluorescent intensity is basically stable; When the FWA solution is set under common daylight lamp, the fluorescence intensity retains stable basically.

The research results show that when FWA is used in the EP, it is only suitable for the application in interior wall coating and not suitable for exposure outdoor.

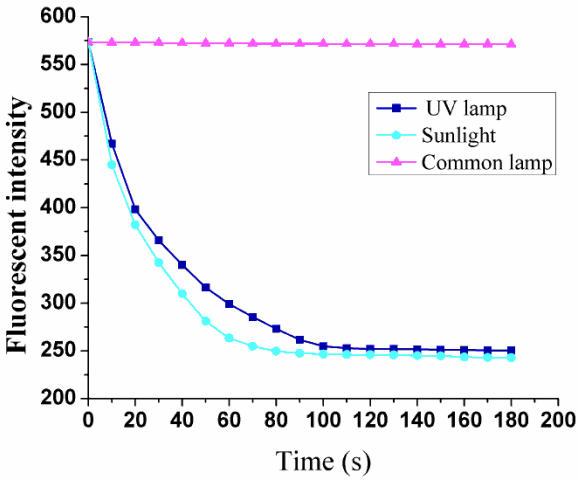

Figure 6. Influence of exposure time on fluorescence intensity

4. **Conclusions**

In this paper, fluorescence spectrophotometer was used to measure the FWA 4BK in household inside wall EP. Excitation wavelength is selected at 347 nm, emission wavelength is selected at 437nm and the measuring temperature is 30℃. Measurement results show that there is a good linearity between the fluorescence intensity and the FWA concentration in the range of 0.025 mg/ml to 0.25 mg/ml. The correlation coefficent is 0.998 and the detection limit is 0.0007 mg/ml. RSD ranges from 0.49% to 0.72% and the percent recovery ranges from 98.3% to 104.5%.

The influence of exposure time and storage time on measurement results are also studied in this paper. The results show that the fluorescence intensity of FWA solution changes obviously under UV lamp and sunlight while keeps stable under the common lamp. When the FWA solution stores for 10 days, the fluorescence intensity reduces by 14.634 which caused the measurement error 0.003mg/ml.

The research results in this paper show that the proposed method implements quantitative analysis of the FWA in EP. During the measurement, the sample should keep away from the sunlight. The measurement should carried on after the sample is configuration completed. We should also pay attention to maintain a constant temperature of the sample. The research results in this paper provides a reliable basis for the research and application of FWA in EP.

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