

The Research on Fluorescence Intensity Attenuation of UV Fluorescent Inkjet Ink

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Abstract

In order to improve the fluorescence lifetime of fluorescent ink, the impacts of illumination time and light intensity on fluorescence intensity attenuation were discussed. Different contents of fluorescent dye were chosen to prepare ink samples and the effect about content of fluorescent dye on fluorescence intensity attenuation was discussed. Different types and contents of UV absorber were chosen to prepare samples respectively and the effect of types and contents of UV absorber on fluorescence intensity attenuation was discussed. The experiments showed that the fluorescence intensity attenuation was significant with extension of light intensity and enlargement of illumination time; content of fluorescent dye had a significant influence on fluorescence intensity attenuation; UV absorber was conducive to improve light resistance of fluorescent inkjet ink, and its content had certain influence on fluorescence intensity attenuation. Fluorescence intensity attenuation was not obvious about the developed ink at the right intensity of fluorescence intensity and illumination time.

Introduction

The present situation of ever-changing and failures to prohibit about fake and inferior goods makes safety anti-counterfeiting printing get more and more attention. In particular, some of the prints pursue a variety of unique artistic effect, which put forward higher request towards printing anti-counterfeiting technology. Driven by a variety of needs, anti-counterfeiting inks which have multiple functions get much more favour, such as UV fluorescent inkjet ink. It is one of the digital anti-counterfeiting technologies which are most widely used [1]. It is made by adding the corresponding of visible fluorescent compounds into the ink-jet printing ink, whose print can inspire the visible light (400-800nm) under UV light (200-400nm) [2]. Compared with the traditional anti-counterfeiting technology, UV fluorescent inkjet ink is not only characterized by simple implementation, low cost, good concealment, abundant colours and convenient inspection, also can enhance artistic effect of print and increase the added value. Fluorescence intensity which determines the quality of anti-counterfeiting performance after forming presswork is one of the most important performance indices of UV fluorescent inkjet ink. At present the fluorescence intensity of the ink in domestic stimulated by UV light gradually weakened and even disappeared over time. Therefore, it has vital significance to research the factors which lead to fluorescence intensity attenuation. Excitation condition and ink components have effect on the fluorescence intensity attenuation, so it has practical significance to research the impacts of light intensity and illumination time, content of fluorescent dye, type and content of UV absorber on the fluorescence intensity attenuation in order to provide theoretical

basis for preparing the UV fluorescent inkjet ink which has high fluorescence intensity and low fluorescence intensity attenuation.

Experiment

Raw and processed materials

Dye: red UV fluorescent powder; Solvent: acetone, butyl acetate; Resin: polyurethane resin (Zhongshan kay trade co., LTD.); UV absorber: UV-531, UV-327, UV-328, UV-7292 (Tianjin Rianlon new material co., LTD).

Experimental apparatus

HJ-6A Digital display constant temperature bull magnetic blender (Jiangsu Ronghua equipment manufacture co., LTD); RF-5301PC Fluorescence spectrometer (Shimadzu international trading Co., LTD); Enotest alpha LM high energy (ATLAS MTT GMBH); Motor coating machine (RK Print Coat Instruments Ltd.).

Preparation methods of ink and coating sample

Resin is scattered in organic solvents and mixed to completely deliquescent by magnetic force. After resting for some time, it will form the evenly scattered and stability carrier. Then the UV fluorescent powder and additives are added into the carrier and mixed to completely deliquescent by magnetic force or water bath to get the UV fluorescent inkjet ink after filtering.

Ink was evenly coated on the substrates using No. 1 wire rod and samples were cut into rectangle about 4.5 mm * 13 mm.

Test methods of fluorescent intensity

Test methods of fluorescent intensity about solution

Quartz colorimetric utensil about 10*10mm is used when fluorescent intensities about solution are tested. Excitation wavelength is set at 365 nm and the slit width of excitation and emission both are 1.5 nm. Scanning speed and sensitivity are respectively set at medium and high.

Test methods of fluorescent intensity about coated samples

Coated samples are directly fixed in test tank of fluorescence spectrometer when fluorescent intensities about coated samples are tested. Coated face orientates towards light source by adjusting position and parameters are the same as them of test methods of fluorescent intensity about solution.

Test methods of light resistance

Enotest alpha LM high energy is used. Parameters: BST =60°C±5°C; CHT=40°C±10°C; E (Radiation energy) =60W/m2,

80W/m², 100W/m²; R·H (Relative humidity) =40%±5%; Rain=No; Number of phases time (max 12)=8.

Results and discussion

Effect of illumination time and light intensity on fluorescence intensity attenuation of UV fluorescent inkjet ink

When emission of the excitation light is continuous at room temperature and the natural environment, each fluorescent group molecular will lose its original ability after launching a certain number of photons, which is named photobleaching [3]. To explore effect of excitation light on the fluorescence intensity attenuation, coated samples are directly fixed in enotest alpha LM high energy and the program is written. Illumination intensities are respectively set at 60W, 80W and 100W. Fluorescence intensities after different illumination times are tested. The result is shown in figure 1.

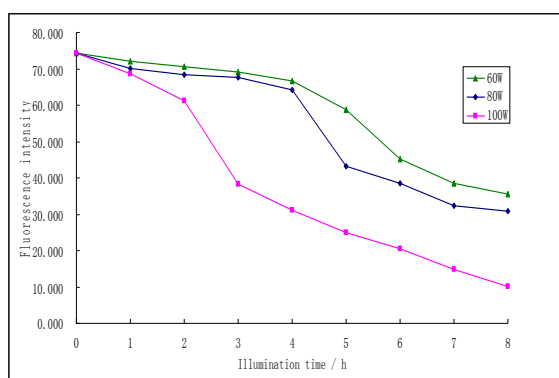


Figure 1 relation between fluorescence intensity and illumination time of samples under different light intensity

The figure 1 shows that when the excitation intensity is determined, law about fluorescence intensity attenuation of fluorescent inkjet ink samples is accordant, namely beginning with slow decay, fluorescence intensity reduces significantly after certain illumination time. With extending illumination time, the number about excitation times of fluorescent molecules will increase under the excitation light. Internal structure of molecular is irreversible changed after emission so that it can't absorb more photons and ulteriorly launch fluorescent, which leads to fluorescence intensity attenuation. When the illumination time is determined, the greater the light intensity, the decline of fluorescence intensity will be more serious and the rate of fluorescence intensity attenuation will increase. Increasing the intensity of excitation light will cause time to stop in excitation area of fluorescence molecular increasing, so photobleaching probability of single fluorescent molecule will be improved and fluorescence intensity attenuation is more likely to happen.

Effect of content of fluorescent dye on fluorescence intensity attenuation of UV fluorescent inkjet ink

Fluorescent dye is one of the most important ingredients of UV fluorescent inkjet ink, and it is critical to show

anti-counterfeiting mark. In order to research the effect of fluorescent dye on the fluorescence intensity attenuation, fluorescent inkjet ink samples about different contents of fluorescent dye are prepared based on the limit of material saturation. Fluorescence intensities after different illumination times are tested. The result is shown in figure 2.

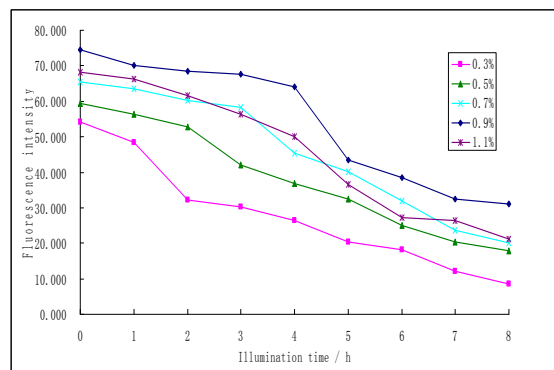


Figure 2 relation between fluorescence intensity and illumination time of samples about different content of fluorescent dye

The figure 2 shows that initial fluorescence intensity of coated sample increases and the rate of fluorescence intensity attenuation reduces with the increase of the content of fluorescent dye. When the content is more than 0.9%, initial fluorescence intensity was worse instead. When fluorescent dye increases, the number of fluorescent center ion increases under the proper deformation force due to luminous particles increasing, which leads to increasing of initial fluorescence intensity. What's more, the number about excitation times is more and the fluorescence intensity attenuation is slow under the same excitation light. When content of fluorescent dye increases to a certain level, it is easy to produce common ion effect. Deformation force is insufficient to impel electronic into the metastable ground state of forbidden band through the valence band [4]. Quenching of fluorescent material happens to cause energy loss, which leads to the initial fluorescence intensity decreasing [5].

Effect of type of UV absorber on fluorescence intensity attenuation of UV fluorescent inkjet ink

In order to improve the light resistance of fluorescent inkjet ink, you can add moderate UV absorber into the system. Molecules of UV absorbers contain chromophore which can absorb UV ray whose wavelength is smaller than 400 nm, such as -N=N-, -C=N-, -C=O-, -N=O-, etc. Chromophore mainly absorbs UV light and converts it into chemical energy, heat and the other light to realize function of shielding UV light[6]. In order to discuss influence on fluorescence intensity attenuation, four different kinds of UV absorbers are selected to prepare samples and fluorescence intensities after different illumination times are tested. The result is shown in figure 3.

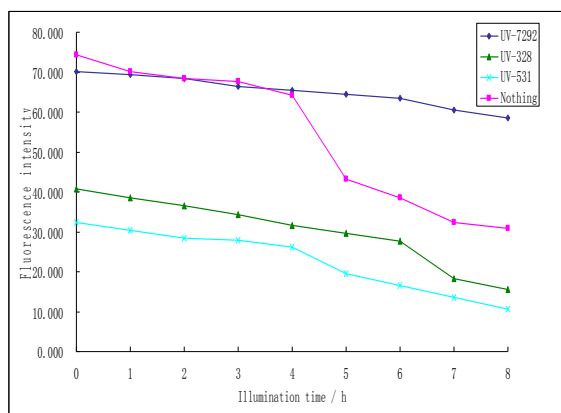


Figure 3 relation between fluorescence intensity and illumination time of samples about different content of UV absorber

The figure 3 shows that fluorescence intensity attenuation of samples including UV absorber is slow and light resistance is good with extending illumination time. Different kinds of UV absorbers have different contribution to the fluorescence intensity attenuation. Nitrogen oxygen free radical generated by hindered amine HALS UV absorber (UV - 7292) can not only absorb UV light from 300nm to 320 nm and reduce the power of excitation light, also has regenerative function in the process of optical stabilization and light stability is better than UV- 328 and UV-531 [7]. The spectral absorption range avoids best excitation wavelength of the red fluorescent ink samples (371 nm), so the impact of UV-7292 on the initial fluorescence intensity is not obvious. Structure of Diphenyl ketone type UV absorber (UV - 531) and benzene and three azole nitrogen ultraviolet absorber (UV - 328) exists hydrogen bonding chelate ring in the intramolecular, after which absorbing UV light from 300nm to 375 nm and from 270nm to 380 nm, photo-interconversion causes the light energy turning into heat energy. The energy absorbed is costed and return to the initial molecular, which can reduce the rate of fluorescence attenuation and initial fluorescence intensity.

Effect of content of UV absorber on fluorescence intensity attenuation of UV fluorescent inkjet ink

The impact of UV absorber (UV-7292) on the fluorescence intensity is small, but it can improve the light resistance of fluorescent inkjet ink. In order to discuss effect of content of UV absorber on fluorescence intensity attenuation, different contents of coating samples including UV absorber (UV-7292) are prepared and fluorescence intensities after different illumination times are tested. The result is shown in figure 4.

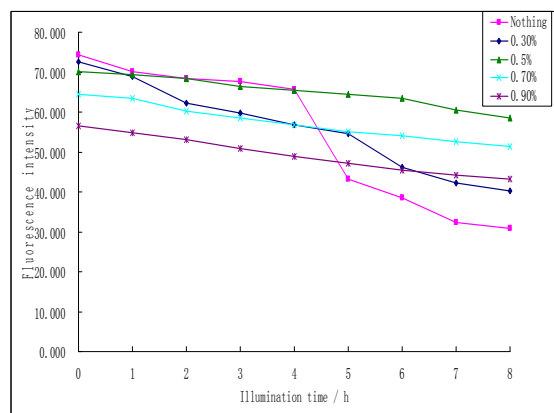


Figure 4 relation between fluorescence intensity and illumination time of samples about different content of UV absorber(7292)

The figure 4 shows that with the increase of content of UV absorber (UV-7292) initial fluorescence intensity decreased obviously, rate of fluorescence intensity attenuation is slow and the decline of fluorescence intensity with the illumination time extension is not obvious. When its content is more than 0.5%, the change of fluorescence intensity attenuation rate is small. With content of UV absorber (UV - 7292) increasing, the number of free radical generated and reduction degree towards light power will increase. The number about excitation times of fluorescent molecules will increase so that the phenomenon of fluorescence intensity attenuation will be improved. When its content increases to a certain degree, initial fluorescence intensity is too low and the limitation of UV absorption ability make the rate of fluorescence intensity attenuation no longer changed. Comprehensive consideration, when content of UV absorber (UV-7292) is 0.5%, the effect is best.

Conclusion

- 1) Fluorescence intensity decreases significantly and the rate of fluorescence intensity attenuation increases with extending of illumination time and increase of light intensity.
- 2) Initial fluorescence intensity increases and the rate of fluorescence intensity attenuation decreases with the increase of the content of fluorescent dye. When the content is more than 0.9%, initial fluorescence intensity was worse instead and the rate of fluorescence intensity attenuation is slow.
- 3) Fluorescence intensity attenuation of samples including UV absorber is slow and light resistance is good with extending illumination time. The type of UV absorber has a significant influence on fluorescence intensity attenuation. The impact of UV absorber (UV-7292) on the fluorescence intensity is small, and the fluorescence intensity attenuation is not obvious.
- 4) With the increase of content of UV absorber (UV-7292), initial fluorescence intensity decreased obviously, rate of fluorescence intensity attenuation is slow and the decline of fluorescence intensity with the illumination time extension is not obvious. When its content is more than 0.5%, the change of fluorescence intensity attenuation rate is small. when content of UV absorber (UV-7292) is 0.5%, the effect is best.

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