Analysis of UV-LED curing technology and existing problems of varnish for printed matter

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Abstract. UV-LED curing varnish is more environmental. In order to let people understand UV-LED curing varnish and existing problems of UV-LED curing technology and provide reference and theoretical basis for the future development of UV-LED curing varnish, the paper sketched basic composition of UV-LED varnish and curing process and pointed low initiation efficiency and slow curing speed were the main problems of the UV-LED light curing technology through referring to a large number of documents and related data. The solutions are suggested: First, the photoinitiators with absorption spectra matched to emission spectra of LED should be selected; second, monomers with more functional groups should be used.
Keywords: UV-LED varnish; photoinitiator; curing speed.

1 Introduction

With the improvement of living standards, people are increasingly seeking high quality packaging. Glazing oil is also known as varnish or glazing paint. It is a colorless, transparent or translucent ink [1]. Coated varnish in the print surface will improve the gloss, water resistance and wear resistance of print. It is able to protect the print, make the print more gorgeous and also convenient for subsequent processing of print [2]. According to the different curing technology, currently varnish on the market can be divided into oily varnish (solvent based varnish), water-based varnish and UV varnish [3]. From the angle of environmental protection, solvent-based varnish will gradually be replaced by water-based varnish and UV varnish. The water-based varnish is easy to get dirty and has slow curing speed and other shortcomings. But UV varnish has considerable development because of its fast curing speed, without solvent evaporation, green environmental protection and other advantages. However, traditional UV light curing generally adopts high-voltage mercury lamp and metal halide lamp light source. It would increase high energy consumption, large emissions of thermal and ozone and other issues, which have caused some adverse effects to the UV varnish development. With the development of science and technology, a more environmental friendly curing technology of UV-LED varnish has become a research hotspot in recent years [4]. In the present paper, the basic composition and the problems of UV-LED varnish are reviewed.

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2 Overview of UV-LED curing varnish

UV-LED is the abbreviation of ultraviolet light emitting diode.UV-LED light source uses the photoelectric conversion principle, electron and the positive charge in the chip collide and bind into light energy in the moving process, making the UV-LED curing more energy saving, environmental protection, and long light source life, low radiation heat [5-6].UV-LED curing varnish is usually composed of prepolymer, monomer, photoinitiator and promoter [7].Under the action of the UV-LED light source, monomer and prepolymer make the varnish change from the liquid to the solid product through the cross-linking polymerization.

Prepolymer, also known as oligomer, constitutes the basic skeleton of varnish, is a film forming material of varnish system, and determines the basic properties of varnish. Prepolymer commonly used includes unsaturated polyester, epoxy acrylate, polyurethane acrylate, polyester acrylate, polyether acrylate, and so on [8].

Monomer, also known as active diluent, constitutes binders of varnish with prepolymer and influences the rheological properties of UV varnish and properties of the cured film. It not only regulates polymerization degree, viscosity and curing velocity of varnish system, but also adjusts some physical properties such as the chroma, gloss and density. The viscosity and curing speed of different monomers are affected by the different functionality [9]. Generally the higher the functional degree is, the faster the curing rate is, but the worse the dilution effect is. Commonly used monomer: Monofunctional monomers, namely 2-hydroxyethyl methacrylate (HEMA), Cyclic Trimethylopropane Formal Acrylate (CTFA), 2-(2-Ethoxyethoxy) ethyl acrylate(EOEOEA), 2-Phenoxy Ethyl Acrylate (PHEA), N,N -dimethyl-2-Propenamide (DMAA); Bis-functional monomer, namely 1,6-Hexanediol diacrylate (HDDA) and Tripropylene glycol diacrylate (TPGDA), Dipropylene glycol diacrylate (DPGDA), Diethyleneglycoldimethacrylate (DEGDMA); Trifunctional and a polyfunctional monomer, namely Trimethylolpropanetriacrylate (TMPTA), Ethoxylated (5) pentaerythritoltetraacrylate (PPTTA), Trimethylolpropanetrimethacrylate (TMPTMA), Propoxylated (6) trimethylolpropanetriacrylate (TMP6POTA).

Photoinitiator, after UV irradiation, absorbs energy to the excited state, forms free radicals or ions, and initiates the unsaturated double bond of monomer and prepolymer to polymerize. The polymer molecules are continuously cross-linked to form a network structure. Until the free radical activity is completely ran out, the chain growth will be over. So the varnish can be completely solidified [10]. As a result, the photoinitiator plays an important role in the varnish curing.

While promoter, an integral part of the varnish system, is accounted for a smaller proportion in the varnish system, the effect on the performance of the varnish is more important. Due to inherent characteristics of UV-LED curing, some common promoters cannot participate in light curing reaction then stay in the cured film, which will cause some defects such as pinhole, anti-sticking oncured film. So the active promoters participating in the curing reaction should be selected as far as possible when choosing promoters. The leveling agent and wax powder are more used, and mainly regulate the flow of varnish and smoothness.

3 Problems and countermeasures during the development of UV-LED curing varnish

3.1 Problems

(1) The slow curing speed of UV-LED does not match the printing speed. At present, the printing speed of offset printing has reached the 18000 sheets / h (240m / min) and that of intaglio printing is 300~350m/min. UV high speed printing systems which speed up to 300m / min has reached the practical level [11]. Since the coating and curing process of varnish is on-line printing, it is very important to increase the curing speed of UV-LED varnish.

(2) Lack of photoinitiators with absorption characteristic fitting into the narrow emission spectrum of the UV- LED lamp

UV-LED curing process was developed from the UV curing process, the traditional UV curing uses the entire UV wavelength light of 200~450nm. However, most UV-LED curing concentrates in the 395~405nm wavelength, only a few concentrates in the 365nm wavelength [12]. Currently on the market, UV-LED curing products mainly have two main types of wavelength, wavelengths of 365nm and 395nm. In the same type of products, 395nm wavelength peak intensity is larger than 365nm. 365nm wavelength is short and its energy is high, leading to local overheating, seldom application. So wavelength of mainstream of UV-LED curing application is still 395nm on the market. To achieve the better curing speed, absorption spectra of photoinitiators have to fit into the narrow emission spectrum of LED lamp. Photoinitiators applied in UV curing before is no longer applicable for UV-LED curing, in other words, currently the initiator strong absorbing in 395-405nm is lacked.

3.2 Countermeasures

Most traditional UV curing light source are the high pressure mercury lamp and metal halide lamps, The emission spectra is wide, continuous and greatly different from the emission spectra of LED.Figure 1 is a comparison of spectral irradiance and UV-LED high pressure mercury lamp.

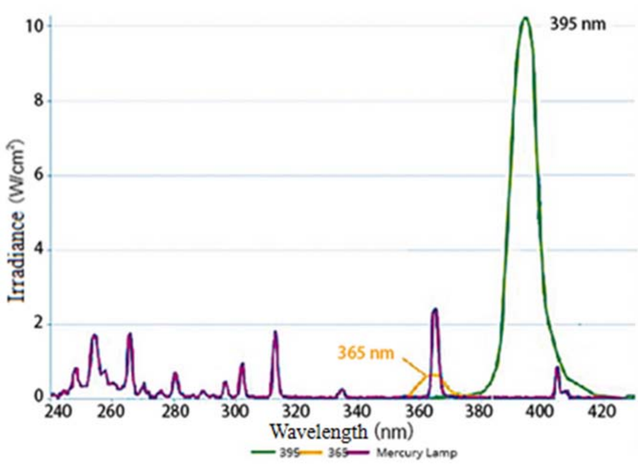

Figure 1. The spectral irradiance of UV-LED and high pressure mercury lamp

Figure 1 is a spectral irradiance comparison of UV-LED and high pressure mercury lamp [11]. The emission spectrum distribution of high-voltage mercury lamp was continuous, and for the LED, based on the limits of the forbidden band width of the semiconductor material in element, although the spectral energy is very strong, the wavelength distribution is extremely narrow; Light energy strength emitting from LED specific spectrum is stronger than that from the same spectral of traditional light sources [13]. But from the integral light of the whole emission spectra speaking, LED is not as good as high-voltage mercury lamp; In the same types of products, comparing with 365nm light, the power / area (peak irradiance) produced by 395nm UV-LED light source is 10 times than the former. So the key and difficult point is to select the appropriate photoinitiators for developing UV-LED varnish. Considering the possibility of band overlapping, one or more photoinitiators (or more likely is photoinitiator combination) should be studied to provide enough free radicals and initiate the efficient polymerization.

One of the factors that we must be considered when selecting photoinitiators is that the absorption spectrum of the photoinitiators needs to match with the emission spectrum of the light source. Because emission spectrum of high-voltage mercury lamp light source is continuous, conventional UV varnish solidifies in the UV light source of wide band (250nm to 420nm), more photoinitiators can be selected. Combined photoinitiators have good absorption reaction with different wavelengths of ultraviolet light, which can achieve the fully curing of varnish surface layer and the deep layer. However, the photoinitiators reacting under the ultraviolet light emitting from UV-LED light source are less. Therefore, it is necessary to select photoinitiators with excellent reaction performance [14].

UV-LED light source emits a specific narrow band ultraviolet light, so photoinitiators of UV-LED varnish not only require the stronger absorption capacity and reaction efficiency, but also their absorption band need to match with emission wavelength, which can realize the curing of varnish layer on the surface and in the interior at the same time [4]. Therefore, when choosing photoinitiators of UV-LED varnish, we should ensure photoinitiations have the best absorption characteristics at specific wavelengths of UV-LED light source, meanwhile we also should develop the best ratio of photoinitiators composition to absorb limited ultraviolet light as much as possible, to balance yellowing and curing of varnish [15].

The main absorption range of the most photoinitiators is listed in Table 1. We can see that the main absorption range of the most photoinitiators are below peak wavelength range of 365/395nm of LED light. However, UV-LED light source is not a pure monochromatic, most of photoinitiators have wide absorption band. When only considering the maximum value, they are often ignored. Some of the photoinitiators in 365nm and / or 395nm or above region are not absorbed. Table 1 is the absorption peaksof all kinds of common UV photoinitiators.

Table 1. The absorption peaks of all kinds of common UV photoinitiators

Type	Absorption Peak/nm
184	240-250,320-335
651	330-340
369	325-335
907	320-325
819	360-365,405
1173	265-280
2959	275-285,320-330
TPO	350-400
MBF	255,335
784	380-390,460-480
TX	395-430
ITX	258,382
389	368,492

For UV-LED curing varnish, in order to achieve a better effect of initiation and curing, it is necessary to select photoinitiators which absorption peak are more than 365nm, such as TPO and 819. Although the absorption peak wavelength of 784 is longer, but the price is so high that it is used less on the market. Moreover, because the amount of residual migration of 184, 907, 1173, MBF, ITX and other photoinitiators is large, their photolysis products are toxic and harmful to the human body and the environment, so they are disabled in the cigarette package and food packaging, etc. Toxicology studies show that ITX, as a fat soluble compound, through the strong force between the cell phospholipid layers, can affect the movement and hardness of cell membrane, may have an impact on the body's endocrine hormones. In addition, two kinds of photoinitiators BP and 4-MBP have also been shown to have carcinogenic effects, skin contact toxicity and reproductive toxicity. In Europe, trace of ITX was tested in Nestle milk powder in 2005. The reason was that the photoinitiator ITX residues contained in the UV ink in Nestle milk powder packaging materials caused the contamination of milk powder due to migration [16]. Currently Omnipol TX, Omnipol 910, IHT-PI 389 and other environmental products in the UV-LED photoinitiators are available for using.

In addition, most UV-LED curing varnish adopts silk screen and offset printing. In order to improve curing speed and curing effect, we can get down to reconstructing the screen printing and offset printing machine. The ways to solve the problem of poor curing effect of the LED curing currently include retaining a group of mercury lamp from three group of standard mercury lamp of original offset printing machine, installing LED light source curing system and combining the UV curing mercury lamp with LED light curing. After the improvement of the technology of the prepolymer, initiator and active monomer for varnish, the traditional UV curing system would be completely replaced by UV-LED curing.

LED curing with low energy consumption requires high reaction activity curing varnish system. Along with the progress of the raw materials, new hyperbranched high reaction oligomer, for example, Sartomer CN 2303, alkoxylate multifunctional acrylate oligomer, and multi-functional groups monomers, and new photoinitiators with maximum absorption peaks in 395~405nm will be developed and applied inUV-LED curing system. The curing rate and the curing film performances of UV-LED varnish would be improved.

4 Conclusions

The UV-LED curing with characteristics of efficiency, no emissions of VOC, ozone and Hg as well as low process temperature will gradually replace the traditional high pressure mercury lamp curing. Namely, UV-LED curing varnish will replace traditional UV curing varnish and become development trend of the varnish market in the future. However, in the development process of UV-LED curing varnish, the low efficiency of photoinitiations and slow curing speed are the key problems. Now market urgently need the photoinitiators with maximum absorption in the wavelength of the 395~405nm. By improving raw materials properties and optimizing formulation, the aim of increasing the curing speed and enhancing the properties of curing film and promoting the development of print finishing processing technology could be reached.

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