Research on the Performance of UV-Curable Screen Printing Watermark Varnish

Beiqing Huang[*1], Si Wang[*2], Wei Yuan[*1], Xianfu Wei[*1]

[*1]*Beijing Institute of Graphic Communication, Beijing, China*

[*2]*Institute of Chemistry Chinese Academy of Sciences, Beijing, China*

Email：Corresponding author: huangpeiqing@bigc.edu.cn

Abstract: In this work, based on the ultraviolet (UV)-curable screen printing watermark system, the watermark varnish was prepared by changing pre-polymer, monomer and photoinitiator respectively. The permeability, refractive index, curing speed and screen printing effect of the watermark varnish were investigated. The results show that the permeability and refractive index of varnish were affected by the specific weight, refractive index and volume fraction of monomer or prepolymer. The bigger the specific weight and refractive index are, the better the permeability of varnish is. Proper monomer functionality and initiator content can improve the curing speed of varnish. The comprehensive performance and screen printing effect of the prepared varnish are admirable.

Keywords: UV-curable screen printing watermark varnish; Refractive index; Permeability; Curing speed

1. Introduction

As a useful anti-counterfeiting method, watermark is applied in some particular products which are highly demanded in anti-counterfeiting. Because of its long periodicity, no flexibility of pattern designing, complex processing, and expensive cost, the conventional watermark is limited in applications except only for mass production [1]. Recently, printing watermark technique which is used to print the watermark on paper is becoming more and more important due to its advantages of low-cost, simply operating, mature printing processing, and so on. The technique solves the drawbacks of conventional watermark process and keeps its advantages in anti-counterfeiting, which thus make it be applied widely.

The mature printing technique provides good external conditions for printing watermark, thus the research about watermark varnish become the key point to realize the printing watermark technique. Recently, UV-screen printing watermark which combine UV-curable watermark varnish with screen printing is used in printing watermark [2]. UV-screen watermark varnish is mainly composed of monomer, prepolymer, and photoinitiator, and their effects on the performance of varnish will be useful in investigating more practical UV-watermark varnish.

2. Experimental

2.1. Materials

Prepolymer: 6311－100，EB870

Monomer: EOEOEA、NPGDA、DPGDA、TMPTA、PO3-TMPTA

Photoinitiator: 1173

2.2. Instruments

- Paper surface absorption weighing instrument ZBK-100,China
- Abbe refractor WAY-2W,China
- Ultraviolet（UV）curable equipment Fusion Light Hammer 6，USA
- FTIR-8400，SHIMADZU
- Cone-and-plate viscometer Brookfield CAP 2000+，USA

2.3. Methods

2.3.1. Preparation

The watermark varnish samples were prepared by mixing and stirring its components homogeneously according to the equation.

2.3.2. Testing Method of the viscosity

Measure the viscosity of watermark varnish sample using cone-and-plate viscometer with a torque of $200s^{-1}$.

2.3.3. Testing Method of the refractive index of liquid

Measure the refractive index of liquid sample with the Abbe refractor.

2.3.4. Testing methods of the watermark varnish Permeability

Measure the permeability of watermark varnish by paper surface absorption weighing instrument. In the testing environment with temperature 25℃ and humidity 65%, fix the offset paper (70 g/m^2) to determine the initial weight. Attach the back of paper closely to watermark varnish for 300 seconds, after sucking and pressing the paper, measure its weight immediately. The permeability can be present by the increase weight of paper. As the equation (1) shows:

978-1-935068-36-5 © 2010 SciRes

$$C = (g_2 - g_1)\,F \qquad (1)$$

In the equation (1), C is the increase weight of paper; g_2 is the paper weight after permeation; g_1 is the original weight of paper; F is the testing area of 100 cm^2.

2.3.5. Testing methods of curing speed

Represent the curing speed with the conversion rate of C=C double bond. Cure the watermark varnish sample with UV-curing equipment at the power of 120 w/cm and speed of 20m/min. Test the IR with FT-IR and calculate the conversion rate of double bond. As equation (2) shows:

$$C_r = \frac{A_0 - A_x}{A_0} \times 100\% \qquad (2)$$

In the equation (2), A_0 is the absorption spectrum intensity ratio of 810 cm^{-1} band and 1730 cm^{-1} band without UV irradiation, A_x is the absorption spectrum intensity ratio of 810 cm^{-1} band and 1730 cm^{-1} band with UV irradiation for a certain time. C_r is the conversion rate of double bonds. The higher the conversion rate of varnish is, the faster the curing speed is when the varnish was exposed in the UV light with special wavelength.

3. Results and Discussion

3.1. The effect of monomer on the function of watermark varnish

Five usual monomers were used with their main properties shown in table 1. Adjusted the ratio of monomer/prepolymer, and the viscosity of varnish was controlled within 3000±10mPa.s. Measured the viscosity, refractive index, and conversion rate of double bond under proper radiations of varnish by changing the monomers, the results were shown in figure 1～3.

Table 1. The properties of monomers

monomer	functionality	refractive index	viscosity (mPa.s, 25℃)	specific gravity (g/cm^3)
EOEOEA	1	1.4366	6.9	1.013
DPGDA	2	1.4502	10.3	1.052
NPGDA	2	1.4503	10.8	1.031
PO3-TMPTA	3	1.4590	123.0	1.050
TMPTA	3	1.4723	124.9	1.109

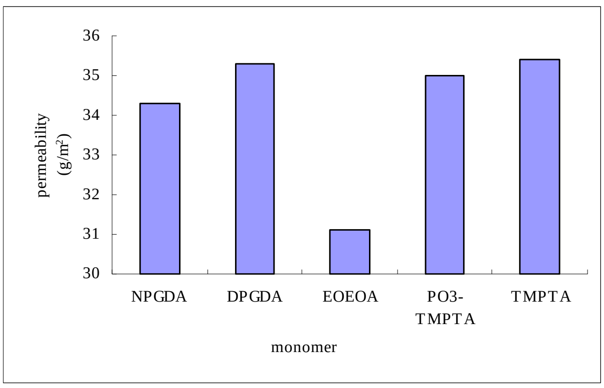

Figure 1. The effect of monomers on the permeability of watermark varnish

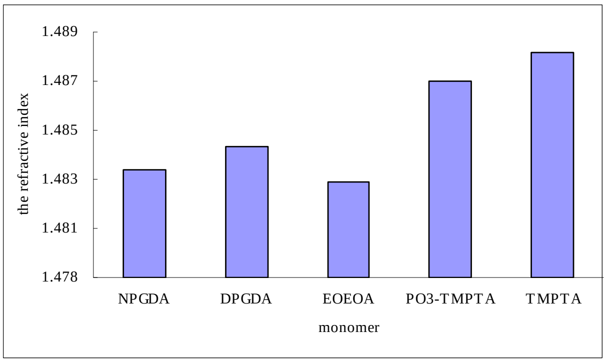

Figure 2. The effect monomers on the refractive index of watermark varnish

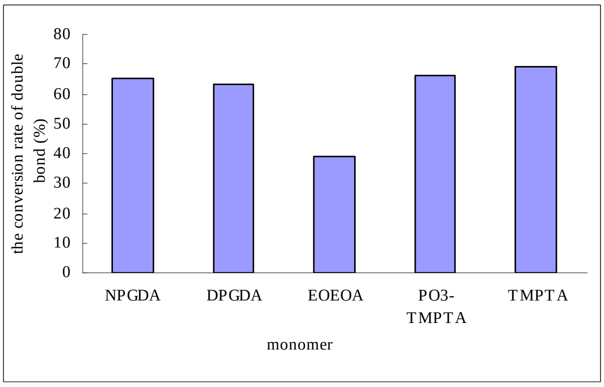

Figure 3. The effect of monomers on the conversion rate of double bond of watermark varnish

The permeability is one of the most important parameters of watermark varnish. Within a proper range, the bigger the value of permeability is, the better the result is. Figure 1 shows that monomers affect the permeability, and their order is: TMPTA>PO3-TMPTA>TMPTA>DPGDA>EOEOA. For the same type of components, the permeability is stronger when the specific gravity is bigger, which is due to its bigger gravity. From figure 1, we can see that the permeability of watermark varnish increased with the specific gravity of monomers.

The refractive index is another important parameter of watermark varnish. Only when the refractive index of watermark varnish is close to that of paper fiber, the printing watermark effect will be fine. The figure 2 shows that the refractive index of watermark is not obviously affected by the monomers while the value of the mixture is larger than that of monomers, which indicates the refractive index of watermark varnish is related with the components. In the ideal condition, that is the mixed volume is equal to the addition of the monomers, and the mixture is transparence, the refractive index of mixture can be calculated by the following equation:

$$\frac{1}{n}=\frac{1}{\sum_{i=1}^{m}V_i}\sum_{i=1}^{m}\frac{V_i}{n_i} \qquad (3)$$

$$Vn^{\frac{2}{3}}=\sum_{i=1}^{N}V_i(n_i)^{\frac{2}{3}} \qquad (4)$$

In equation (3), (4), n is the refractive index of mixture, V_i is the volume fraction of monomer i, n_i is the refractive index of monomer I [3][4]. The results calculated by (3), (4) is similar to the experimental results. It can also be known that the refractive index of monomers and its content in mixture obviously affect the refractive index of watermark varnish. Therefore, in screen varnish, the monomer has little affection on the refractive index of watermark varnish due to its low volume fraction. In total, the watermark effect can be well presented by applying the above five monomers in the watermark varnish.

From figure 3, we can see that the monomers have a great affection on the curing speed of watermark varnish. The curing speed of watermark varnish prepared by EOEOEA is lowest, and that TMPTA is fastest. The density of the functionality is responsible for the phenomenon. When the density is higher, the possibility of functionality to react is higher and thus the curing rate is faster [5]. EOEOEA has only one (methyl) acrylic group, and does not react to crosslink, and therefore the curing velocity is slow. On contrary, TMPTA has three groups, and its curing rate is fast.

3.2. The effect of prepolymer on the properties of watermark varnish

Prepolymer A(6311-100) and B(EB870) were used, and their properties are listed in table 2. Only changing the ratio of prepolymer/monomer, the permeability, refractive index and the conversion rate of double bonds under proper radiation were measured, which were shown in figure 4～6.

The figure 4 shows that the permeability of watermark varnish varies little because of the similarity of specific gravity of the two prepolymers.

The figure 5 shows that the refractive index of watermark varnish also varies little due to the similarity of the refractive index of the prepolymers. In this case, the value is maximum when the ratio is A: 4B. According to equation (3), (4), the lower the refractive index of prepolymer

Table 2. The properties of prepolymers

prepolymer	refractive index	vicosity （mPa.s, 25℃）	Specific gravity (g/cm³)
6311-100	1.489	8100	1.061
EB870	1.492	48000	1.073

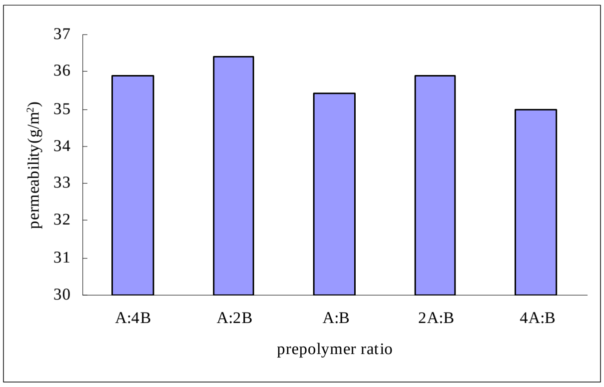

Figure 4. The affection of complex prepolyers on the permeability of watermark varnish

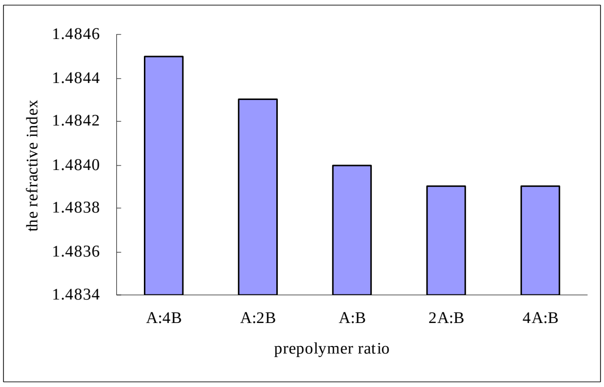

Figure 5. The affection of complex prepolymers on the refractive index of watermark varnish

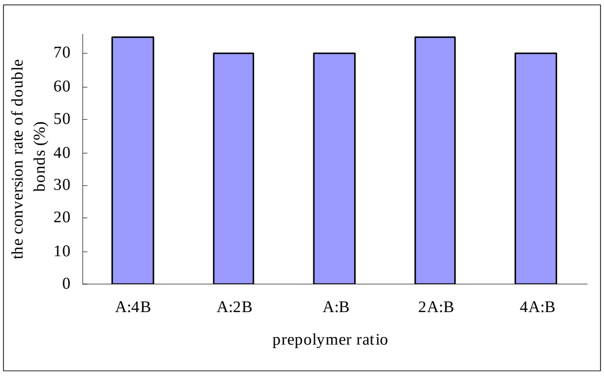

Figure 6. The affection of complex prepolymers on the conversion rate of double bonds of watermark varnish

is, the lower the refractive index of watermark varnish is.

The figure 6 presents the conversions rate of double bonds for the prepared watermark varnish sample with different ratio of prepolymers are basically 70%, which is attributed to the same functionality of A(6311-100) and

978-1-935068-36-5 © 2010 SciRes

B(EB870) with six groups. Therefore, the curing speed is not affected by the ratio of the two prepolymers.

3.3.The affection of the contents of photoinitiator on the curing speed

Keeping the components and viscosity of watermark varnish, the conversion rate of double bonds under proper radiation is measured by changing the content of initiator 1173, which is shown in figure 7.

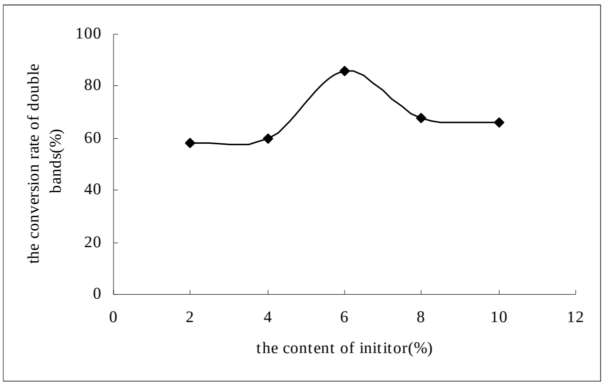

Figure 7. The affection of the content of initiator on the conversion rate of double bonds

The figure 7 shows that in the low range of 1173, the conversion rate of double bonds increases with the increment of 1173, which can be attributed to the proportion of free radical to the initiator. In low concentration, the free radical is low, and the curing speed is also low. The curing speed does not increase until the content of 1173 reached up to 6%, and then decreases due to the increment of the radical recombination caused by too much free radical [6]. Thus, the concentration of initiator must proper in the UV-watermark varnish.

3.4. The properties of watermark varnish

According to the results above, we prepared the UV-screen watermark varnish with better properties. Its properties are shown in table 3. The picture printed by screen printing with the watermark varnish is also shown in figure8.

It can be seen from table 3 and figure 8 that the properties of the UV-screen watermark varnish is fine, and the patterns are distinguished.

4. Conclusions

In this paper, the following conclusions are obtained:

Table 3. The properties of UV-screen watermark varnish

permeability (g/m^2)	refractive index	The conversion rate of double bonds（%）	viscosity (Pa·s,25℃)
36.8432	1.4839	86	3002

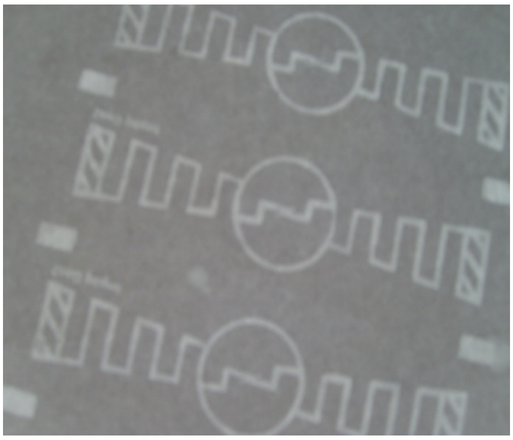

Figure 8. Patterns printed by screen printing with watermark varnish

1. The permeability of UV-screen watermark varnish is affected by the specific gravity of nomomers and prepolymers. The permeability of watermark varnish is better with the increment of specific gravity, and the patterns are better when the permeability is higher.
2. The refractive index of UV-screen watermark varnish is related with the refractive index of monomers, prepolymers and their volume fraction. Relatively, the refractive index of varnish is more affected by the refractive index of the prepolymer with higher volume fraction. The refractive index of varnish is higher, the patter is better.
3. The curing speed of UV-screen watermark varnish is affected by monomers, prepolymers and initiators. The more the functionality is, the higher the curing speed is. In addition, the curing speed keeps increasing with the increment of the content of initiators until it reaches up to 6%.
4. The over-all properties of UV-screen watermark varnish are fine, and the patterns printed with the varnish are distinguished.

References

[1] Liu Zunzhong, Huang Min, Jiang Dongsheng, "Security printing and application" , Beijing, Printing Industry Press, January 2008.

[2] Allen,et al. "Method of producing a simulated watermark":US,5118526, June 2, 1992.

[3] Zhang Xiong, "Research on the mixed refractive index of various transparent liquid", Journal of Yunan Normal University,(3),1987, pp.69-75.

[4] Zhang Hemin, Ping Ronggang, Liu Changxin, "The refractive index of mixed liquid" [J], Journal of Xinan Normal University, vol.16(2) ,1991, pp.273-275.

[5] Wei Jie, Jin Yangzhi, "UV curable coatings", Beijing, Chemical Industry Press, 2005.

[6] Wu Shikang, "Introduction to Polymer Photochemistry", Beijing, Science Press, 2003.