A New UV Curable Inkjet Ink

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Abstract

The technology of inkjet printing is used in various applications, accomplishing evolution every day, with the trend toward on-demand printing and small lot printing. In particular, the markets of UV curable inkjet have shown growth in various applications, mainly in Europe and North America, because they can be used with nonabsorbent substrates such as plastic films and they fix quickly. The main polymerization mechanisms of UV curable inkjet are free radical polymerization. Because acrylate monomer has abundant raw materials, it can reduce a cost. However the photoinitiators and acrylate monomers in free radical inks can cause strong skin irritation and skin sensitization. We developed a new UV curable inkjet ink with low cost. The newly developed inkjet ink uses a free radical polymerization along with superior safety raw materials. The new ink has good curing properties with good adhesion for plastic films and superior safety.

Introduction

There are two curing mechanisms of UV curable ink which are free radical polymerization and cationic polymerization. We compared these polymerization mechanisms and have selected a free radical polymerization because its raw material is low cost and curing speed is faster.

In this report, the difference between free radical polymerization and cationic polymerization is explained. In addition, we explain the example of the development for the superior safety and adhesion of a new ink.

Comparsion of UV Curing Mechanism

In recent years, many articles and patents on UV curable inkjet ink are publicized. Following table 1 shows comparison of two different UV curing mechanisms. [1] [2] [3]

Curing Mechanism	Free Radical	Cationic
Raw Materials	Acrylate	Epoxy, Oxetane Vinyleter
Kind of Raw Matelials	Many	Little
Curing Speed	Fast	Late
Shrinkage	High	Low
Cost	Low	High
Inhibitor factor	O2	Humidity

Table 1 : Comparison of UV curing mechanisms

In order to make inkjet ink, the low viscosity is required. Therefore, low viscosity acrylate monomers are formulated by the radical polymerization system. The examples of low viscosity acrylate monomers are: Isobornyl Acrylate, Phenoxyethyl Acrylate, Tetrahydrofurfuryl Acrylate, Vinyl Caprolactam, Dipropylene Glycol Diacrylate, and Alkoxylated Neopentyl Glycol Diacrylate. Recently, the case where 2- (2-Vinyloxyethoxy)ethyl acrylate is used abundantly. Following figure1 shows curing mechanism of free radical polymerization.

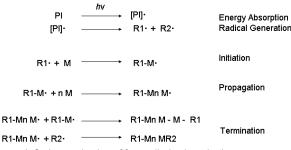
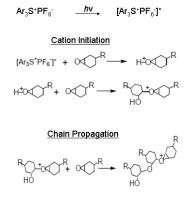


Figure 1. Curing mechanism of free radical polymerization

Generally, these low viscosity acrylics monomers cause strong skin irritation and skin sensitization. For example, if ink or not cured ink touches the skin, it could cause inflammation or allergy. Therefore, workers are restricted and it becomes one of the problems of usability.

On the other hand, the ink which uses cationic polymerization system, uses an epoxy monomer, vinyl ether, oxetane, etc. and those materials are low in viscosity; therefore it is said that it is more suitable for inkjet ink. Following figure2 shows curing mechanism of cationic polymerization.



Photoinitiator Activation

Figure 2. Curing mechanism of cationic polymerization

Epoxy monomer, mainly used by a cationic polymerization system, is weaker skin irritant than an acrylics monomer. In addition, it is skin sensitization or AMES is positive. However, there are some epoxy monomers which have weak skin sensitization. The cost of raw materials of cationic polymerization is usually expensive. Therefore, they still have many issues to overcome before it is used widely in the world.

We compared these polymerization mechanisms and have selected development of free radical polymerization because its raw material is lower in cost and curing speed is faster. We are careful and give special attention to the raw materials safety. We developed a new UV curable inkjet ink which is applicable of labeling and packaging markets. This ink has unique characteristics: it has good adhesion on PE and PP films and it has superior safety of raw materials. Concern about the safety of a material is increasing globally now. We think that the usage of our highly safe UV inkjet ink will increase from now on.

Contact Angle

First of all, in order to obtain a high resolution printing on the substrates of labels and packages, the ink should spread. We evaluated the wettability over a base material using numbers of different raw materials with superior safety. The result is shown in Figure 4 and 5.

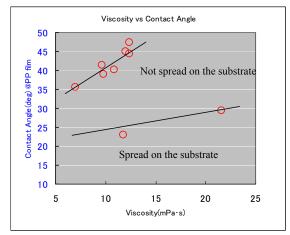


Figure 3. Viscosity vs Contact Angle

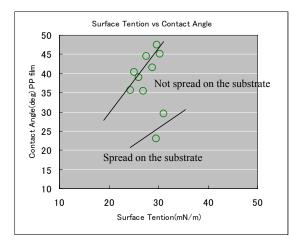


Figure 4. Surface Tension vs Contact Angle

The viscosity and surface tension of raw materials have to be optimized because they are related to the characteristics of spreading on the substrates. We developed an ink using raw materials with the sufficient spread on the substrates.

Shrinkage

In order to use ink for a label and a package application, the sufficient adhesion to the substrates is required. Therefore, we developed an ink with improved adhesion. As compared with cationic polymerization, a free radical polymerization is inferior in substrates adhesion because shrinkage of a free radical polymerization is higher. Therefore, we developed an ink with small cure shrinkage. The photograph before improvement of cure shrinkage and after improvement is shown in Figure 5 and Figure 6 respectively.

Figure 5 shows the curing ink on the substrate before cure shrinkage improvement; it turns out that the substrate has curled greatly due to shrinkage.

On the other hand, Figure 6 shows that the substrate has no curl which is due to improvement of cure shrinkage.



Figure 5. Before improvement of shrinkage



Figure 6. After improvement of shrinkage

Ink Adhesion

The experimental results are shown in Figure 7. We tested adhesion between several different kinds of substrates and Cyan ink. We obtain superior adhesion in PP and PET substrates which is typically used for a label and a package; we also realized superior adhesion with Polycarbonate and PVC.

Kind of Substrates	Cross Hatch Test
Polypropylene Film	
PET FILM	
Polycarbonate	
PVC	

Figure 7. Adhesion test results of developed cyan ink

Ink Properties

Following table 2 shows a summary of developed ink properties.

Table2 : Developed ink properties

	Developed Ink	
Safety Data of Raw Materials	Primary Irritant Index <2 Skin Sensitization(OECD406) Negative AMES Negative	
Viscosity	8-11 mPas@ 25 degree	
Surface Tension	24 -28 mN/m @ 25 degree	
UV Curing Speed	100 – 200 m/min @ UV Lamp 200W/cm	
Adhesion (Polypropylene Film)	Excellent *Test method Scotch Tape test	
Adhesion (Polyester Film)	Excellent *Test method Scotch Tape test	
Adhesion (Polycarbonate)	Excellent *Test method Scotch Tape test	
Adhesion (PVC)	Excellent *Test method Scotch Tape test	

In conclusion, we have developed a super adhesive and highly safe UV inkjet ink which is highly suitable for label printing and package printing industry.

References

- N.Caiger and S.Herlihy: Oxgen Inhibition Effects in UV-Curing Inkjet Inks, IS&T's NIP 15: International Conference on Digital Printing Technologies, 116-119 (1990).
- [2] A.Tomotake, T.Takabayashi, N.Sasa, A.Nakajima, and S.Kida, Proceedings of NIP24: International Conference on Digital Printing Technologies and Digital Fabrication 2008, 532-534 (2008).
- [3] M.Ishibahi, Y.Hotta, T.Ushiroguchi, R.Akiyama, K.Ohtsu, H.Kiyomoto and C.Tanuma: Photocurable inkjet ink for printing on metallic and plastic substrates. IS&T's NIP 23, 134-137 (2007).

Author Biography

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