

An In-situ Formed Cross-linked Coating and Its Effectiveness as Under-layer in Laser Imaging ^a

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Abstract

This paper relates to a process for preparation of a coating soluble in aqueous alkaline solution, which didn't dissolve in almost all organic solvents and neutral water. The coating composition comprises a poly(acrylic acid-diacetone acrylamide) and isonicotinyl hydrazide as the cross-linking agent. The two components were dissolved in 3-methoxypropanol to prepare the coating solution, which was applied to a grained and anodized aluminum substrate and then dried at 110 °C to obtain the final coating. There exists intermolecular hydrogen bond between the pyridine ring of the cross-linking agent and the carboxylic acid of the polymer. Furthermore, the in-situ chemical reaction between the hydrazide group and the carbonyl group provided the hydrazone bond during drying. The co-action of the physical and chemical cross-linking rendered the coating insoluble in general organic solvents. However, when the coating was exposed to aqueous alkaline solution, the hydrogen bond was broken immediately due to the ionization of the carboxylic acid group, leading to quick dissolving of the coating. The coating might be used in the pretreatment of the aluminum substrate of CTP plates or as the under-layer for the production of double-layer imaging system, and was found very effective in promoting the aqueous alkaline solubility of non imaging area upon development after laser imaging.

Introduction

CTP is the direction of graphic arts technology evolution and has become dominant in professional sectors. CTP is a big family of different members, including CTPlate, CTPress, CTProof and CTPaper. Out of them, CTPlate is believed to be the ultimate destination of prepress technology evolution and imposes a great challenge on CTFilm technology, which is the current mainstream in prepress [1-4]. Computer-to-plate (CTP) systems today all work very well. They differ in features, speed, automation, and can reliably image a plate and produce a high quality printable dot. In china, the market has been shifting for CTP technology, and the output of CTP plate in 2011 was about 100 million square meters, which grew than last year 20 %. A number of institutes and companies are engaged in designing and developing CTP plates, among which thermal laser imaging plates appear to be the major direction.

However, for the currently widely used thermal laser imaging CTP plates, there still exist some problems both in production and in the process of using, such as decreasing sensitivity during storage and necessity of pre-delivery aging process, etc. These defects deduce production efficiency and inconvenience to the future operation. There may be several ways to cope with these problems: (a) improving the formula of the heat-sensitive imaging layer, (b) developing new heat-sensitive imageable element, and (3)

special treatment of the substrate, such as introducing a functional bottom coating on the substrate, etc.

The goal of this paper is to design a double-layer heat-sensitive imageable element, wherein a functional copolymer was used for the production of the under layer and an IR dye-containing novolak coating was used as the top layer. Through the study on the effect of the functional under layer on the performance of the positive-working thermal CTP plate, we may find a method to improve the overall performance, including peak sensitivity at 830 nm infrared diode laser, the stability of imaging performance and developing latitude and so on.

Experimental

Reagents and Methods

Acrylic acid (AA), diacetoneacrylamide (DAAM), azodiisobutyronitrile (AIBN), isonicotinyl hydrazide and all organic solvents were commercial products from Beijing Chemicals Co. AA was purified by vacuum distillation before use. FTIR spectra were obtained with a Shimadzu FTIR-8400 infrared spectrophotometer. Film thickness was measured with a Taylor Hobson FTS-S3c instrument. Laser imaging process was performed on a RCTP-1S laser (830 nm) imaging apparatus (Beijing Print Technology and Trade Co. Ltd). Micrograph was obtained on a VHX-600 microscope. Dissolving dynamics of the coatings were measured with a home-made apparatus according to a reported procedure [5].

Synthesis of poly(acrylic acid-diacetone acrylamide) (Poly(AA-DAAM))

In a 250-ml flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet was placed 10.0g of AA, 30.0 g of DAAM, 0.4 g of AIBN and 60 ml of ethanol. The mixture was purged with nitrogen and stirred for 1 h until it became clear. Then the mixture was heated to 65 °C and kept at the temperature for 6 h. The mixture was cooled to room temperature and poured into 500 ml of water. The white precipitate was collected, fully washed with water and dried in vacuo at 80 °C for 16 h. FTIR (film, cm⁻¹)•3378•2971, 2932, 1707, 1655, 1542, 1450, 1363, 1156.

Preparation of the cross-linked poly(AA-DAAM) coating

The cross-linked poly(AA-DAAM) coating was prepared according to the following process: 1.5 g of poly(AA-DAAM) and 0.54 g of isonicotinyl hydrazide were dissolved in 7.5 g of 3-methoxypropanol to obtain a clear solution. 3-5 drops of crystal violet solution (5 wt.% in 3-methoxypropanol) was added to the solution which was then spin-casted at 300 rpm on the top of an

aluminum plate and dried at 110 °C for 10 min. FTIR (film, cm^{-1})•3378•2971, 2932, 1707, 1655, 1592, 1542, 1450, 1363, 1156.

In order to facilitate comparison, poly(AA-DAAM) coating without isonicotinyl hydrazide were also prepared in accordance with the same process. The dissolving behaviors of the polymer coatings were measured and compared under identical experimental conditions.

Preparation of double-layer heat-sensitive positive CTP plate and imaging performance

The double-layer CTP plate was prepared as follows: (a) applying a first coating solution (10 wt.% in 3-methoxypropanol), comprising poly(AA-DAAM) and isonicotinyl hydrazide (the weight ration of poly(AA-DAAM) to isonicotinyl hydrazide is 2.8:1) on an electro-chemically grained and anodized aluminum plate; (b) drying at 110 °C for 10 min; (b) applying a second coating solution, comprising an IR dye, a novolak resin and 3-methoxypropanol, and (c) drying at a temperature of 110 °C for 10 min.

Then the CTP plate was mounted on the rotating disc of the exposure device for laser scanning, developed with alkaline developing solution. For comparison, a single-layer CTP with the same thermal imaging layer composition and coating thickness was prepared for performance evaluation.

Results and Discussion

Preparation of poly(AA-DAAM) and the crosslinked coating

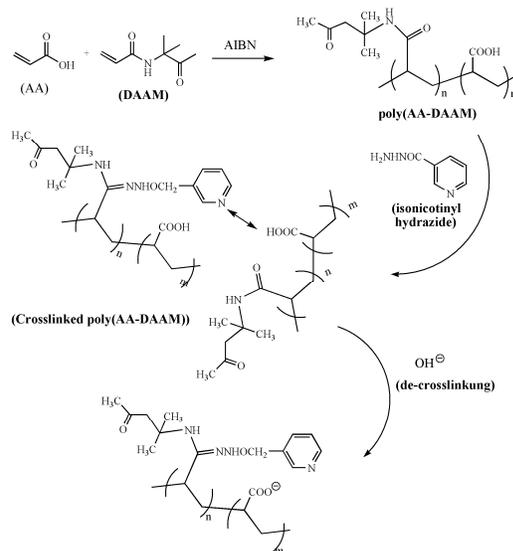
As shown in scheme 1, poly(AA-DAAM) was synthesized through copolymerization of AA and DAAM in the presence of AIBN. The copolymer has two kinds of functional groups, i.e., the carboxylic group and the carbonyl group, which was used to form crosslinked structure through the addition of a functional molecule, isonicotinyl hydrazide. First, weak hydrogen bond was readily formed between the pyridine ring and the carboxylic group. In this stage, poly(AA-DAAM) is still a linear copolymer. Then, in-situ chemical reaction between the hydrazide group and the carbonyl group was initiated at an elevated temperature (110 °C) during the film-forming process, producing a crosslinked polymer structure. Because the hydrogen bonding is noncovalent, the crosslinked structure can be easily broken by alkaline solution through the reaction of the hydroxide ion with the carboxylic group. More over, as a result of the chemical conversion of the carboxylic group into its ionic counterpart, the polymer coating readily became water soluble.

In-situ crosslinking reaction was traced by FT-IR spectra (Figure 1). As shown, the difference between the crosslinked poly(AA- DAAM) coating and the non-crosslinked one is that the former has an weak absorption at 1592 cm^{-1} , which is the characteristic absorption for the newly-formed hydrazone bond. This confirmed that the crosslined polymer film was successfully prepared.

Solubility of the coatings

The in-situ formed cross-linked coating should have poor solubility in general organic solvent, including 3-methoxypropanol which was used to prepare the coating solution. However, the

non-crosslinked coating still should be soluble in 3-methoxypropanol because there is no chemical change during the formation of the coating. To verify this speculation, we measured the dissolution behaviors of the two coatings in 3-methoxypropanol. Here, a homemade apparatus for in situ monitoring film thickness change was used to measure the dissolving rate of the coatings in 3-methoxypropanol [5].



Scheme 1. Synthetic rout of the crosslinked poly(AA-DAAM) and the de-crosslinking process

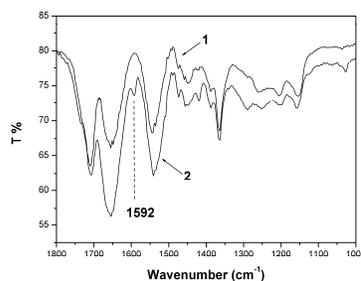


Figure 1. FT-IR spectra of the non-crosslinked coating (1) and the crosslinked coating (2)

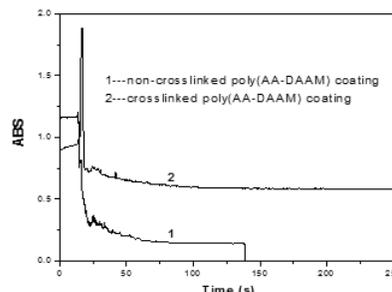


Figure 2. Comparison of the dissolving rate of the coatings (film thickness: about $1\mu\text{m}$; $25\text{ }^\circ\text{C}$)

As seen in figure 2, the ABS value is correlated to the coating thickness. For the non-crosslinked poly(AA-DAAM) coating (curve 1), with the dissolution of the coating, it was getting thinner and thinner and the absorption became weaker and weaker. The dissolving rate was very fast as indicated by the steeper slope of the curve. On the other hand, the crosslinked poly(AA-DAAM) coating (curve 2) was completely insoluble or scarcely soluble in the selected solvent, the absorption intensity (the ordinate value) remained almost the same in the testing process. However, both the two coatings can be easily dissolved in alkaline aqueous solution. For example, the two coatings with a thickness of about 1 μ m could be dissolved in 5 wt.% NaOH water solution in no less than 6 s. The unique feature for the crosslinked poly(AA-DAAM) coating, i.e., poor solubility in organic solvent and excellent solubility in alkaline aqueous solution is helpful to the preparation of the double-layer CTP plate.

Novolak resin + IR dye
Crosslinked poly(AA-DAAM)
Aluminum substrate

Figure 3. Structure of the double-layer CTP plate

A preliminary study on the imaging performance of the prepared double-layer CTP plate

The structure of the double-layer CTP plate was shown in figure 3. There is a “transition layer” (i.e., the crosslinked poly(AA-DAAM) under layer) between the “thermal imaging layer” (the top layer) and the aluminum substrate. No IR dye is present in the under layer. Because the polymer of the under layer is insoluble in 3-methoxypropanol used for preparing the coating solution of the top layer, the under layer should not be affected by the operation of the second coating.

Compared with those “single-layer” CTP plate which don't have an under layer, the double layer CTP may have several advantages: (a) Avoid direct contact of the IR absorber-containing imaging layer with the substrate, thus reduce heat loss during IR laser thermal imaging, (b) reduce the coating thickness of the top layer and the amount of IR dye, and (c) enhance solvent resistance of the coating. In addition, as the under layer is easily dissolved in alkaline water, the double-layer CTP should be easily developed in general CTP developing solution.

Figure 4 shows the patterns of the coatings exposed by 830 nm laser beam, followed by development with alkaline developing solution for 25 seconds. Figure 4 (A) and (B) are respectively assigned to the single-layer CTP plate and the double-layer CTP plate, which were exposed and developed under the same conditions. The white areas represent the aluminum substrate or the exposed areas, and the dark areas are the non-exposed areas. The exposure intensity is about 120 mJ/cm². As seen, both the two plates gave positive images, however, the double-layer CTP plate seems to have a much better performance whether in edge sharpness or in image definition. For the single-layer CTP plate, the exposed areas were not completely developed, that is to say that small amount of the coating resin had not been removed by the developing solution. As for the double-layer plate, the aluminum

substrate was completely exposed, showing higher sensitivity. It is likely that the double-layer structure contributes to the imaging performance of the heat-sensitive plate. This should be good for practical application.

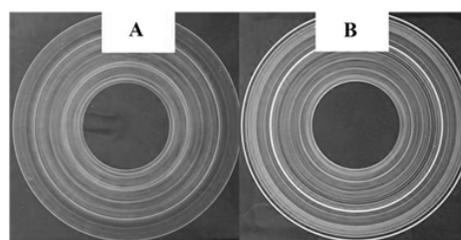


Figure 4. Photograph of the patterns of the single-layer (A) and the double-layer (B) CTP plate after exposure and developed in 7 wt.% sodium metasilicate aqueous solution for 25 s at 25 °C

Conclusions

A functional copolymer, poly(AA-DAAM), was synthesized and used to prepare the crosslinked resin coating. The coating is insoluble in general organic solvents, but can be easily dissolved in alkaline aqueous solution. This unique feature makes it possible for application in a double-layer CTP plate as the under-layer coating. A preliminary study showed that double-layer CTP plate showed enhanced performance in comparison with the corresponding single-layer counterpart. This study might provide a method for overcoming the weakness of the present thermal CTP plates and further increasing performance. Moreover, because the under layer has excellent resistance to general organic solvents, it is possible to make CTP plate suitable for ultraviolet radiation curing ink.

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Author Biography

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