A Study on the Effect of a Surfactanct Additive on the Performance of a Thermo-sensitive Imaging Material

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Abstract

This paper is concerned with the improvement of the combined properties of a phenolic resin-based thermal imaging composition. A surfactant-like additive, stearamide, was introduced to the imaging material. When drying, the surfactanct material will move to the surface of the thermo-sensitive film to form a very thin layer due to the low surface energy. The thin layer was the so-called monolayer. It can be broken by the infrared laser and developed together with the resin of the exposed area. However, the unexposed area will be protected by this thin layer. As a result, the difference between the exposed area and unexposed area became larger, and the image tolerance and image quality were improved.

Keywords: Stearamide; monolayer; image tolerance

Introduction

CTP has been a hot topic in the printing industry and highlighted in all international and local industrial shows since DRUPA95. 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. There is no doubt that CTP is the direction that the graphic arts technology evolution is heading and it will become dominant in all professional sectors. The market has been shifting for CTP technology. In china, the output of CTP plate in 2008 was 61 million square meters, which grew than last year 72.18%. CTP technology is believed to be the ultimate destination of prepress technology evolution [1~3]. So, a number of institutes and companies are engaged in designing and developing CTP plates, among which thermal laser imaging plates seem to be the major direction. The goal of this paper is to study the effect of a surfactant-like additive on the performance of a positive-working thermal CTP plate in an effort to improve the peak sensitivity at 830 nm infrared diode laser and increase the image of tolerance and so on. In addition, a homemade apparatus for monitoring film thickness change in dissolving were used to evaluate the solubility change of thermo-sensitive imaging material.

Experimental

Reagents and Methods

Phenolic resin (Mn: 20,000), stearamide, crystal violet, infrared radiation sensitive dye (IR dye) and organic solvents were obtained from Beijing Chemicals and used without further purification.

Ultraviolet-visible (UV-vis.) spectra were recorded on a UV-2501PC 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. Contact angle was measured at 25 ^{o}C with a JY-82 optical goniometer (Chengde Testing Machine Co. Ltd., China). Dissolving dynamics of the coatings were measured with a home-made apparatus according to report procedure [4].

Preparation of thermal-sensitive coating and IR laser-induced thermo-imaging performance

Phenolic resin (2.50 g), crystal violet (0.03 g), IR dye (0.06 g) and varied amount of stearamide (0 mg, 26 mg, 52 mg and 78 mg) were dissolved in a 3:1 mixture (w/w, 20 g) of 2-ethoxyethanol and butanone. After mixing and just before coating, the mixture was filtered through a Gelman filter (0.22 μm). The filtered solution was coated using a conventional wire wound rod to a wet thickness of about 20 μm on both quartz plate and one-faced anodized aluminum support. The coatings were dried in an oven for ten minutes at 70-80 °C. The resulting blue coatings comprised a heat-sensitive imaging layer on aluminum or quartz glass substrate.

The sample was mounted to the rotating disc of the IR laser (830 nm) exposure apparatus for laser scanning. Finally, the imaged sample was processed with 0.5 mol/l sodium hydroxide solution.

Results and Discussion

The effect of the amount of stearamide on the quality of the coating films

Table 1 shows the four thermal-sensitive imaging layers comprising different amount of stearamide, i.e., sample 1, 2, 3 and 4. The weight percent of the samples ranged from 0-0.3%.

Table 1 Recipe of the heat-sensitive imaging layers

	Stearamide (mg)	Weight percent	Phenolic resin/ Crystal violet / IR dye (g)
1	0	0.00	2.50 / 0.03 / 0.06
2	26	0.10	
3	52	0.20	
4	78	0.30	

It is know that phenolic resin, crystal violet and IR dye are polar materials because of the presence of phenolate or ionic groups in their molecular structures. However, stearamide, a long chain carboxylic acid amide, is a surfactant-like compound. The long carbon chain is non-polar group. Therefore the miscibility of the blends will greatly affect the quality of the dry layers. Figure 1 shows the surface topography the four layers. As seen, uniform coatings were obtained for sample 1 and 2 (Figure 1-1 and Figure 1-2, respectively). However, in the case of sample 3 and 4 (Figure 1-3 and Figure 1-4, respectively), their coatings were quite inhomogenous, and obvious phase separation can be found. The miscibility of stearamide and the matrix resin (phenolic resin/crystal violet/IR dye) is not so good, and when the weight percent of stearamide was above 2%, stearamide should form detectable separate phase. Figure 2 depicts the possible interaction between stearamide and phenolic resin molecules. The hydrophilic "heads", amid groups, interact with phenolate group through hydrogen bond, while the hydrophobic tail groups assemble far from the stearamide/phenolic resin surface. Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer [5]. The drive force for this process is that the long aliphatic chain could produce a lower surface-energy film. On the other hand, if the adding amount of stearamide is higher than that is need for forming a single monolayer, extra stearamide molecules will present in the matrix of the film, which might pose a problem for film forming. That is what we found in sample 2 and 3. For this reason, sample 1 (stearamide-free) and sample 2 (comprising 0.1% stearamide) were selected to evaluate the effect of stearamide on the performance of the heat-sensitive coatings.

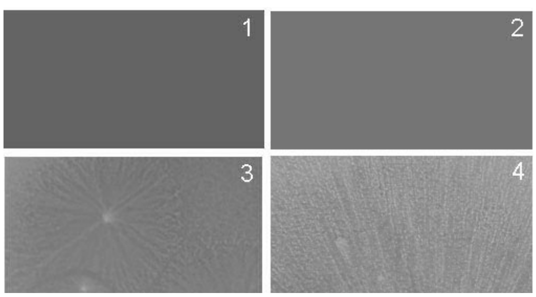

***Figure 1.** The surface topography of sample 1(1), sample 2 (2), sample 3 (3) and sample 4 (4) on aluminum substrate (50 times)*

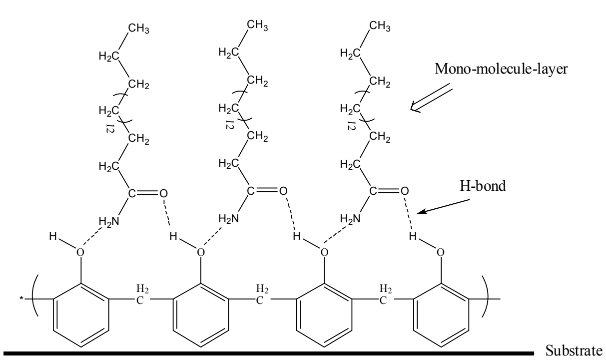

***Figure 2.** Schematic diagram of intermolecular hydrogen–bonding between stearamide and phenolic resin and molecule-layer formed along film surface*

Stearamide effect on the dissolution of the coating films

The effect of stearamide on the solubility of the coating films in alkaline water was estimated according to the results of sample 1 and sample 2. The films were prepared onto quartz glass plates. A self-made apparatus was used to measure the dissolving rate of films in a selected solvent by monitoring film thickness change [4]. Here, 0.5 mol/l sodium hydroxide solution was chosen as solvent. The theory of the apparatus was based on Beer's law. The linear relationship between absorbance and concentration of an absorbing species implies that the absorbance of the film was related to the film thickness and the dissolving rate can be reflected by the change of absorbance. The results were shown in Figure 3.

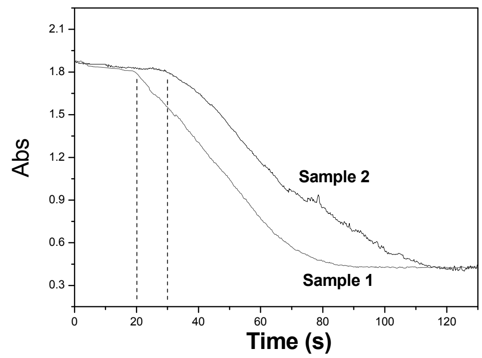

***Figure 3.** Comparison of the dissolving rate of sample 1 and sample 2 films (film thickness: 22 nm)*

There are some differences in dissolution behaviour between the two films. The onset dissolution times were 20 s and 30 s for sample 1 and sample 2, respectively. The phenomenon is related to different compositions of the films. Small amount of stearamide existed in sample 2 depressed its dissolution. It is likely that a stearamide monolayer had formed at the film surface and retarded the permeation of sodium hydroxide solution. This suggestion was supported by the measurement of the contact angles of the films with water, which were 79^o and 86^o for sample 1 and sample 2, respectively. Stearamide monolayer reduced (as shown in Figure 2) the surface tension of sample 2 film.

IR laser-induced imaging performance of sample 1 and 2

The purpose of this study was to investigate the possibility of improving the imaging performance and (or) tolerance of a heat-sensitive CTP plate simply by adding a surfactant-like additive (stearamide) to the imaging composition. Although the additive was used in very small amount, it played an important role in modifying the surface properties and increased the resistance against alkaline developing solution. Furthermore, when the heat-sensitive CTP plate was imaged by IR laser beam, the IR-absorbing dye converted the infrared energy to heat, vaporizing or ablating or destroying the thin stearamide monolayer, while the non-exposed area remained intact. The addition of stearamide could enlarge the difference of alkaline solubility between the exposed and non-exposed areas. As a result, the stearamide-modified heat-sensitive CTP plate should exhibit better imaging tolerance and might be easier to operate.

Figure 4 shows the patterns of the coatings processed by exposure (830 nm IR laser), followed by development with dilute alkaline solution for 20 seconds or 40 seconds. The exposure dose was about 120 mJ/cm^2. The white areas are the aluminum substrate or the non-exposed areas, and the dark areas are the exposed areas. Figure 4 (1) and (2) are imaged sample 1 and sample 2 plates, which were treated in alkaline water solution for 20 seconds. It can be found that both the two plates generated positive images with acceptable quality. When the two imaged plates were developed with the same alkaline water solution for 40 seconds, sample 1 couldn't withstand the corrosion of alkaline developing solution and part of the non-exposed area were dissolved, however, sample 2 still gave fine image as before. It is certain that stearamide contributes to the imaging tolerance of the heat-sensitive plate, which should be good for practical application.

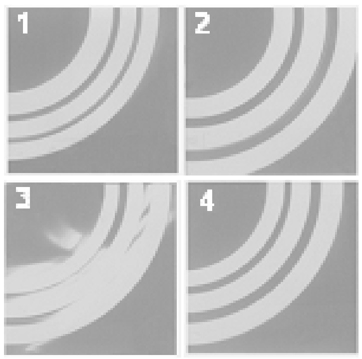

Figure 4. *Photograph of the patterns from sample 1 (1, 3) and sample 2 (2, 4) coatings (thickness: about 2.5 μm) developed in 0.5 mol/L sodium hydroxide solution for different periods of time. 1and 2: for 20 seconds; 3 and 4: for 40 seconds*

Conclusion

A normal heat-sensitive laser imageable composition was prepared and modified with a surfactant-like additive, stearamide. Its effects on film forming property, surface properties, dissolving behavior and imaging performance were fully studied. Results showed that small amount of stearamide would have great influence on the overall properties of the heat-sensitive film.

References

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Author Biography

Li Zhongxiao received his MS degree from Huazhong University of Science and Technology in 2000 and PhD (in Polymer Chemistry) from Institute of Chemistry, Chinese Academy of Sciences in 2003,then joined Beijing Institute of Graphic Communication as an associate professor. Research Interesting: new functional polymers and their properties as information recording materials, including core-shell nanoparticles, thermo-sensitive polymers and photosensitive polymers.