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Study on Hydrophobization of a Thiol Compound on Silver Surface of CTP Printing Plate

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A thiol compound with a long hydrocarbon chain was introduced into the developing solution for a silver chloride DTR printing plate. It was found that the hydrophobicity of physically developed silver area could be greatly improved. The higher the silver density and thiol concentration were, the greater the hydrophobicity of the silver surface was. Raman and XPS study revealed that hydrophobization was caused by adsorption of the thiol compound on physically developed silver particles on the plate.

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Introduction

Computer-to-Plate (CTP) technology provides a preferable way for printing with high speed and quality compared to traditional printing technologies. The number of installed CTP systems over the world has been increased almost at the rate of 100% per year since DRUPA'95.[1] Various printing plates for CTP have been proposed and marketed by many companies.[2] Typical ones are Silverlith SDB (Du Pont Co., based on Silver Halide Diffusion Transfer Reverse [DTR] principle), CTX (Polychrome Co., based on silver halide-PS hybrid system), N90 (Agfa-Gevaert Co., based on photosensitive polymer), and Pearl Gold (Presstec Co., based on thermal-blaze principle). Among the previous four types, the silver halide plate based on the DTR principle is most sold at present. This type of plate is similar to a combined negative–positive film. During development the exposed silver halide is chemically developed to silver, meanwhile the unexposed silver halide is dissolved in the form of complex ions and transferred to a positive layer, where the silver complex ions are reduced and deposited by physical development. The physical developed silver is oleophilic to printing ink and used for producing the image on printing. Much research has been carried out to improve the oleophilicity of the unexposed area. Mercapto-compounds are inclined to be adsorbed onto a metal substrate. When the other ends of the compounds comprise functional groups, different properties could be introduced.[3–5] Various mercapto-compounds have been claimed in the patent literature in connection with surface treatment for lithographic printing.[6,7]

In this article, a thiol compound with a long hydrocarbon chain was introduced into the developer solution. The oleophilicity of the plate was expected to be improved by the hydrophobicity of the hydrocarbon chain. For this reason, the effect of the thiol compound on development was first observed and monitored with a one-dimensional Charge Coupled Device (CCD) to confirm whether the introduction of the thiol compound would be harmful to development or not. Then, water contact angles on the surface of the plate were measured to characterize the hydrophobicity. Finally, the status of the plate surface was further investigated by Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

Experiments

Experimental Plate Preparation

An antihalation layer containing hydroquinone and Metol was first coated on plastic-coated paper. After the antihalation layer was dried, a silver chloride emulsion layer sensitive to green light was coated on top of it. These two layers comprised the so-called "negative film" of the plate. The total thickness was approximately 1~2 µm. After the two layers were hardened, a colloidal solution of PdS was prepared as physical developing nuclei, by mixing solutions of $PdCl_2$ and Na_2S, then was spread over the surface of the emulsion layer. This nuclei layer was called the "positive film" of the plate, and its thickness was thinner than 0.1 µm.

Activation Solution

The activation solution here was made of potassium hydroxide (0.180 mol/L), sodium sulfite (0.400 mol/L) and sodium thiosulfate (0.020 mol/L). The thiol compound, included in the activation solution, is 2-mercapto-7-heptyl-1,3,4-oxidazole. Its molecular structure and Raman spectrum are shown in Fig. 1.

CCD Instrument

Under red light, the reflectivity of the plate was found to change with the amount of silver formed during de-

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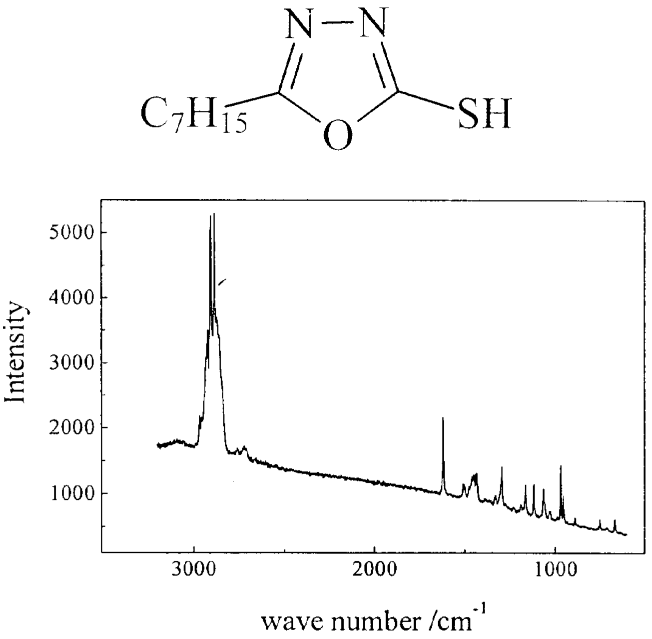

Figure 1. Molecular structure and Raman spectrum of the thiol compound.

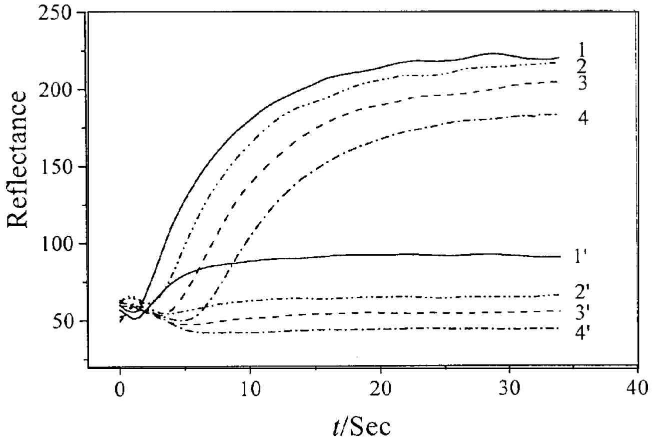

Figure 2. Developing kinetics of the DTR plate in activator with different concentrations of thiol compound. The thiol concentrations of curves 1, 2, 3, 4 are 0, 1.07, 2.14, 3.21($\times 10^{-3}$)mol/L respectively. 1, 2, 3, 4 correspond to unexposed areas, 1', 2', 3', 4' to exposed areas.

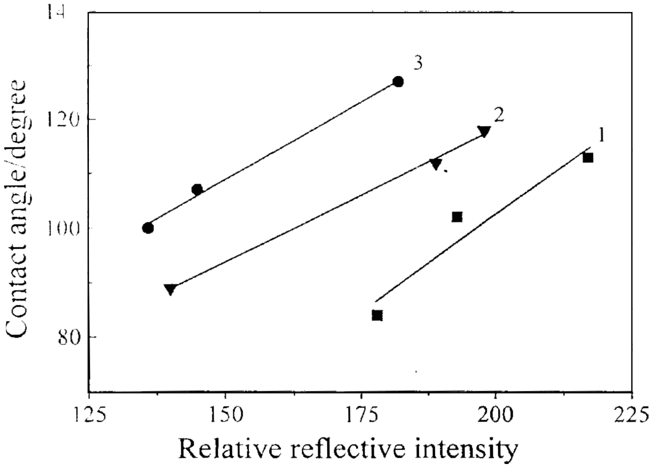

Figure 3. Relationship between contact angles and silver densities developed with different concentrations of thiol compound. The concentrations in curves 1, 2, 3, are 1.07×10^{-3}, 2.14×10^{-3}, 3.21×10^{-3} mol/L, respectively.

velopment. It could be measured relatively and monitored by a one dimensional CCD array in situ and real time with an integral time interval of 200 ms. It was also well known from our previous work[8,9] that the reflectivity was proportional to the developed silver density, hence the developing process could be kinetically described with a reflective intensity-time curve from which the induction period corresponding to the minimum reflective intensities, and the maximum silver density could be conveniently obtained.

Measurement of Contact Angle

Water contact angles on plates were measured by the Beckman method. When a water droplet with a volume (V) of several microliters was put on a horizontal surface of the developed plate, its projective diameter (2r) could be measured by microscopy. Then, the contact angle θ could be calculated according to the following equations.[10] When $\theta < 90°$

$$V/(2r)^3 = \pi/48(3\tan\theta/2 - \tan^3\theta/2) \qquad (1)$$

When $\theta > 90°$

$$V/(2r)^3 = \pi/24(2 - 3\cos\theta + \cos^3\theta) \qquad (2)$$

Raman Spectrum and XPS

A Renishaw1000 type of Raman spectrometer was used to study the surfaces of the plate. XPS was performed on an AXIS HSi spectrometer with the radiation power of 300 w and normal angle to plate surface.

Results and Discussions

Effect of the Thiol Compound on Development

With different concentrations of thiol compound in the activation solution, the developing processes on exposed and unexposed areas were monitored and the results are shown in Fig. 2. When there was no thiol in the developer solution, the silver density in the unexposed area increased rapidly after an induction period of 1 s. When the thiol compound was added to the activator solutions, the induction periods were prolonged to 3-6 s and the maximum silver densities were slightly reduced with increasing thiol concentrations. These results showed that the thiol compound had a small inhibiting effect on development. The acceptable concentration range of thiol compound was found to be $0.5\sim2.5 \times 10^{-3}$ mol/L.

Improvement of Hydrophobicity

Experimental plates were developed in the activation solutions with different concentrations of thiol compound. Water contact angles were measured after the developed plates were washed and dried. As shown in Fig. 3, there was a linear relationship between contact angles and silver densities, i.e., the relative reflective intensities, which meant that the contact angles became greater as the developed silver densities rose, as shown by curves 1, 2, 3, respectively. In addition, it could be also seen from these curves that at an identical devel-

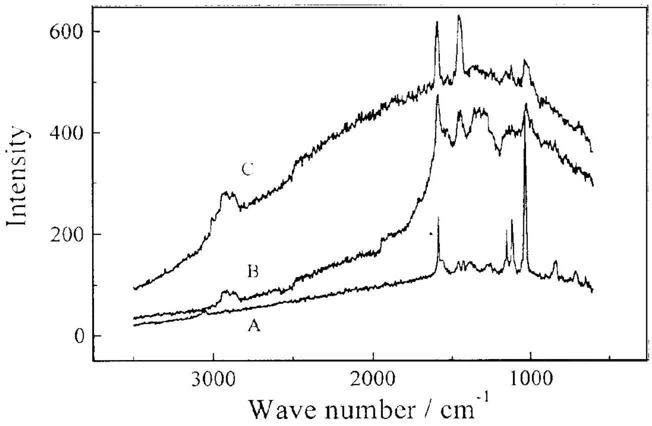

Figure 4. Raman spectra for unexposed areas of plates prepared via different processes. Plate A: developed in developing solution without thiol compound. Plate B: treated with thiol compound solution after the same procedures as Plate A. Plate C: developed in developing solution with thiol compound.

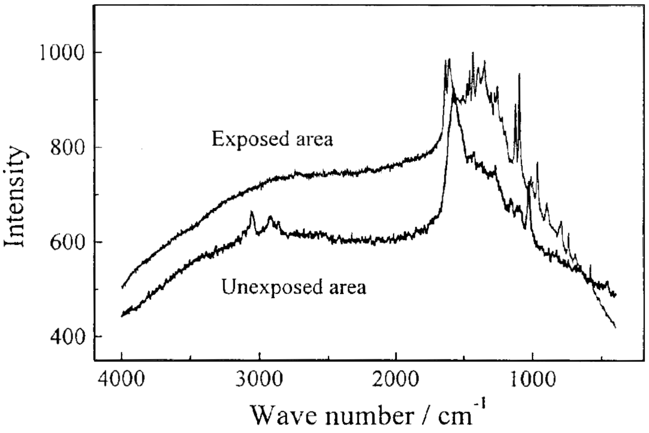

Figure 5. Raman Spectra for exposed and unexposed areas of sample plate C.

TABLE I. XPS Analyses of DTR Plates.

Plate*	N	O	C	S
A	10.6	21.8	57.1	5.9
B	12.1	20.5	58.5	7.3
C	12.0	19.3	57.1	11.7

*Plate A, B and C have the same meanings as those in Fig. 4

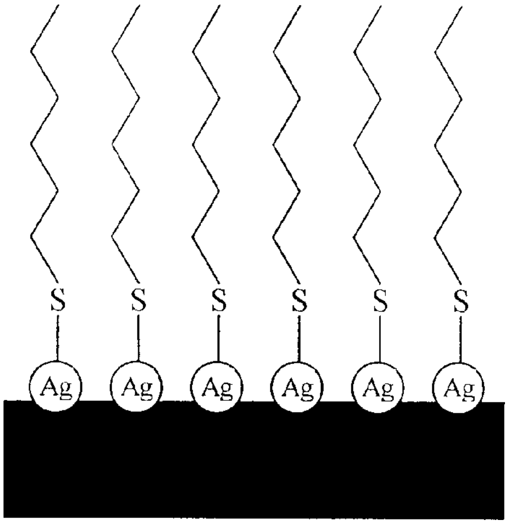

Figure 6. Adsorption model for the thiol compound on silver image.

oped silver density, the higher the thiol concentrations in the developing solution were, the greater the contact angles, i.e., the stronger the hydrophobicity at the developed silver surface. Perhaps more thiol was adsorbed by the developed silver under these conditions.

Study of Plate Surface with Raman Spectroscopy and XPS

As an effort to seek the explanation for improvement of hydrophobicity, investigations on the plate surfaces were carried out with Raman and XPS. Three plates were studied: reference plate A, which was processed in activator solution without thiol compound; standard plate B, a reference plate dipped into an ethanol solution of the thiol compound for 30 s; and sample plate C, which was developed in an activator solution with thiol compound. The Raman spectra of the unexposed areas of these three plates are shown in Fig. 4. The characteristic absorbance (2830–2970cm^{-1}) of a long hydrocarbon chain appeared in the spectra of plates B and C, as in the Raman spectrum of the thiol compound itself, shown in Fig. 1. Therefore, we deduced that the compound had been adsorbed onto the unexposed areas of plates B and C. When a comparison between the Raman spectra of the exposed area and the unexposed area of the plate C was made, as illustrated in Fig. 5, it could be seen that the characteristic absorbance only appeared in the unexposed area, not in the exposed area. This result showed that the thiol compound was only adsorbed on the unexposed area of the plate, where the physically developed silver was deposited.

The composition of the surfaces of plates were analyzed with XPS, and the results are listed in Table I. The sulfur content on the surfaces of B and C was higher than for reference plate A. Obviously, it arose from the adsorbed thiol compound.

Combining the Raman spectra with XPS data, it was reasonable to infer that improvement in hydrophobicity was caused by the adsorption of thiol compound onto the physically developed silver. When the plate was developed in the developing solution in the presence of the thiol compound, the compound would be adsorbed onto the surface of silver particles. This adsorption might take place through a linkage between Ag and S because heavy metal elements are strongly thiolphilic. An adsorption model, therefore, may be proposed as follows: a few or many long hydrocarbon chains of thiol molecules parallel to each other stand vertically on the surface where physically developed silver is located and make up a hydrophobic layer, as illustrated in Fig. 6.

Because the hydrophobicity was related to the adsorption of the thiol compound, certainly it would be affected by the silver density and by the thiol concentration. When the concentration of the thiol compound was higher, there should be many more molecules available to be adsorbed; in addition when the silver density was higher, there should be many more sites available to adsorb thiol compound. In both cases, the adsorption of thiol compound would be increased, thus providing a reasonable explanation of the results in Fig. 3.

Conclusions

1. The thiol compound has a slight inhibiting effect on physical development of the silver DTR printing plate. The induction period was prolonged and silver density decreased.
2. Hydrophobicity of physically developed silver could be improved by the thiol compound. The hydrophobicity increased with increasing silver density and with the concentration of thiol compound.
3. This improvement was attributed to the adsorption of thiol compound onto silver particles.

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