Effects of Toners on Photothermographic Materials Based on Silver Benzotriazole

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Abstract

The photothermographic(PTG) imaging materials are used as digital hardcopy imaging medium in diagnostic medical field. We obtained the hardcopy image by driving laser or thermal print head on PTG materials based on electronic data. Toners, as the most important of components to provide best image quality, is a compound added to modify the normally yellow-brown color of thermally generated Ag^0 *particles to black. In the paper, the effects of phthalic acid(*H_2PA*) and phthalazine(PHZ) as toners on photothermographic materials based on silver benzotriazole had been studied. The results indicated that* H_2PA *as a toner can promote development in higher pH of system and the promotion increased with the amount of* H_2PA *increased. We also found that the development of silver benzotriazole materials was promoted by the introduction of PHZ, and the promotion was strengthened by increasing the amounts of PHZ. The analysis data of SEM and IR indicated that a silver complex, which was supposed to be easy to transmit silver ions to development center to promote development, have been produced by introducing PHZ into the silver benzotriazole materials. The sharp of silver benzotriazole grains were changed by the silver complexes. The XRD data showed that the silver complexes had the same crystal structures as silver benzotriazole.*

Introduction

Toners were used in photothermographic imaging materials (PTG) to adjust image color and create black metallic silver image. The study on toners was revealed that toners were four roles in toning effects[1]: silver ion extraction; silver ion transport; silver redox potential modification; adsorption and control of metallic silver growth. The most popular toners are phthalic acid(H_2PA) and phthalazine(PHZ) in PTG materials. Maekawa et al reported that H_2PA was the silver ion carrier during thermo-imaging process in PTG system based on silver behenate as silver sources[2]. The recent research result shown that the intermediate StAgAgPA which produced in thermo-imaging process including silver carboxlate and silver phthalate was an unsymmetrical silver complex. It could not only improve silver salt solubility but also change its redox potential in thermal imaging process[3].

Phthalazine(PHZ) is one of the toners used widely in photothermographic system. Many research on PHZ showed that PHZ as a ligand to extract the silver from the dimeric silver carboxylate structure to form a stable, colorless complex of silver acetate[4]. A long chain silver carboxylate complexes with PHZ have been claimed as suitable silver sources for PTG materials[5]. In the case of photothermographic materials constructed from the phthalazine/phthalic acid (PHZ/H_2PA) toner systems, a well-defined silver complex has also been reported[6]. Although the structures and characters of complex which created by toners with silver carboxylates were studied and implied the effects of toners on photothermogrphic imaging process, the mechanism of toners has not been known exactly.

Silver benzotriazole as silver sources were applied in black-white PTG materials early[7]. It also applied in color PTG materials in recent years[8]. In silver photothermographic system, toners must be added to increase solubility of silver carboxylates and improve development because of the poor solubility of silver carboxylates. The solubility of silver benzotriazole is lower than that of silver carboxylates by two orders of magnitude, so silver benzotriazole hardly supported silver ions which easy transfer compared with silver carboxylates during photothermographic imaging process. It was much more important to use toners in silver benzotriazole system. Toners introduced in silver benzotriazole system might enhance solubility of silver benzotriazole and improve development, increase density by created silver complex which was better solubility. We study the effect of toners on photothermographic imaging material based on silver benzotriazole as silver sources in this paper to improve the understanding of mechanism of toners on PTG system.

Experimental

Silver benzotriazole (AgBTA) were prepared by the method in reference 9.

The PTG emulsion were mixed with AgBTA as silver sources, NH_4Br as halogenating agents to form AgBr as photocatalysts, H_2PA or PHZ as toners, PVA as binders and developer. Each of PTG emulsion was dispersed by ball-milled and then coated on substrate as sample. The samples were exposed to white light for 20 sec and developed at 140℃ for 30 sec.

The silver benzotriazole after treated with PHZ solutions were investigated by scanning electron microscope, X-Ray Diffractomer, Fourier transform infrared spectrophotometer.

Results and Discussion

1. Effect of H_2PA on PTG system based on silver benzotriazole

The effect of H_2PA as a toner on PTG system based on silver benzotriazole as silver sources were shown in Table 1and 2. Development density including D_{max} and D_0 were all decreased with increasing the amount of H_2PA in table 1. The pH value of system was also decreased because of acidity of H_2PA. The pH value of the system decreased reduced the ionization of H_2PA and the capability of H_2PA combined with organic silver salt. It led to the amount of silver ion which transferred by toners from silver carboxlate to latent imaging center decrease and development density decrease further. In another way, development density was reduced also because that developing capability of developer decreased with pH in system reduced.

Table 1. The influence of H_2PA on photothermographic imaging materials

H_2PA(mol/100 molAgBTA)	pH	Minimum density (D_0)	Maximum density (D_{max})
0	8.05	0.70	1.36
1.0	6.65	0.60	1.03
2.5	5.97	0.60	0.95
5.0	4.83	0.63	0.88
7.5	4.24	0.65	0.76
10	3.83	0.58	0.73

Table 2. The influence of H_2PA on photothermographic imaging materials (system has similar values of pH)

H_2PA(mol/100 molAgBTA)	pH	Minimum density (D_0)	Maximum density (D_{max})
0	7.69	0.61	0.73
1.0	7.72	0.75	0.98
2.5	7.82	0.81	1.18
5.0	7.80	1.09	2.76
7.5	7.77	1.22	2.76
10	7.69	1.92	3.60

In table 2, the results indicated that development density were all enhanced with the amount of H_2PA increased when pH in system were almost same at about 8. The approximate pH in system led to the similar ionization degree of H_2PA and the similar developing activity of developer. On this approximate pH condition, the more silver complexes were created by H_2PA and silver benzotriazole, the more silver ion might be transported from silver salt to development center to promote development and increase development densities of samples when the amount of H_2PA added into system were increased. Comparing data of table1 with that of table 2, we found that H_2PA as a toner can promote development in higher pH of system and the promotion was increased with the amount of H_2PA increased in PTG materials based on silver benzotriazole.

2. Effect of PHZ on PTG system based on silver benzotriazole

Table 3.The effects of PHZ on silver benzotriazole photothermogrphic materials

PHZ (mol/100mol AgBTA)	Minimum density (D_0)	Maximum density (D_{max})
0	0.62	0.77
1.0	0.69	1.00
2.5	0.71	1.07
5.0	0.81	1.12
7.5	0.84	1.28
10	0.89	1.60

PHZ was another toner used widely in PTG system. The effects of PHZ on PTG system based on silver benzotriazole as silver sources were shown in Table 3. Development maximum densities (D_{max}) of samples were all enhanced without significant increase in minimum density (D_0). Obviously, PHZ as a toner was effective in PTG system and its promotion was enhanced with increasing the amount of PHZ. The more amount of PHZ added into system, the more silver complexes were created by PHZ and silver benzotriazole, the more silver ion might be transported from silver salt to development center to promote development and increase densities of samples.

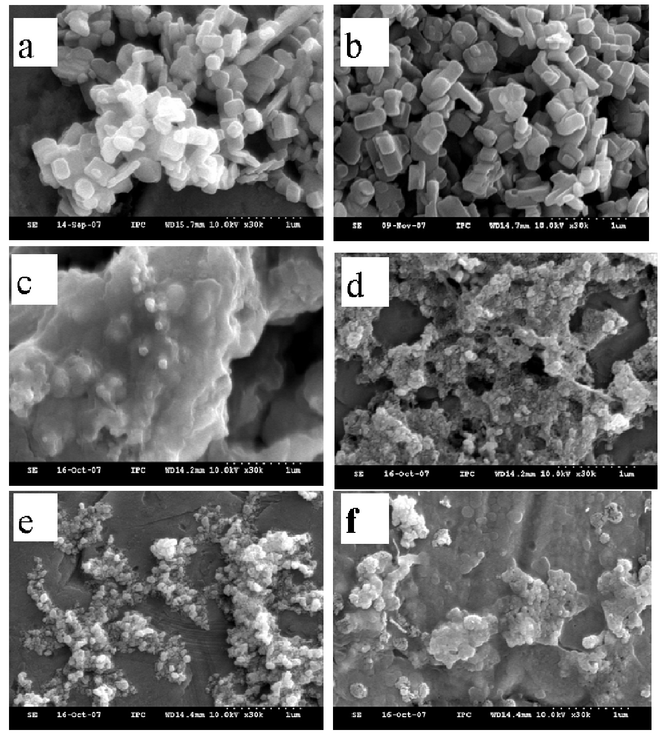

***Figure1**. SEM photographs of AgBTA grains treated with PHZ solutions. Ratio of AgBTA and PHZ (mol:mol). a. AgBTA grains ; b.1:0.1 ; c.1:0.2 ; d.1:0.5 ; e.1:0.7 ; f.1:1*

The SEM photographs of AgBTA grains treated with PHZ solutions were shown in figure 1. The AgBTA grains were visible different in shape before and after it were treated with PHZ solutions. When ratio of AgBTA and PHZ is 1: 0.1, AgBTA grains were almost the same as original AgBTA grain which not be treated with PHZ solution. When ratio of AgBTA and PHZ is 1: 0.2, AgBTA grains were congregated to form big grains on which small grains were appeared. When AgBTA: PHZ=1: 0.5, the small grains increased and the big grains decreased. There were almost small grains in photo (e), big grains were disappeared when AgBTA: PHZ=1: 0.7. Lastly, when AgBTA: PHZ=1: 1, the small grains were aggregated again. These SEM photos showed that the silver complexes which were formed by PHZ and silver benzotriazole increased with the amount of PHZ increased. The silver benzotriazole grains were disaggregated with the silver complexes formed.

The IR spectrum of AgBTA grains after treated with PHZ solution was shown in figure 2. The peak at $2283cm^{-1}$ in spectrum of original AgBTA was attributed to N-Ag vibration in penta-heterocycles salt which created by benzotriazole and silver ion. After AgBTA were treated with PHZ solutions, the peak at $2283cm^{-1}$ was disappeared and a new peak at $2360cm^{-1}$ was appeared. This new peak was attributed to N-Ag vibration in hexa-heterocycle salt which created by PHZ and silver ion. The IR spectrum of AgBTA after treated with PHZ solution were similar to that of Ag-PHZ in the higher wavenumber region (> $2000cm^{-1}$) and almost the same as that of original AgBTA in the lower wavenumber region (< $1500cm^{-1}$). The IR spectrum implied that a new complex, $(AgBTA)_{1-x}/(Ag\text{-}PHZ)_x$, might be formed after AgBTA treated with PHZ solutions. The peak at $2360cm^{-1}$ was weaker with the amount of PHZ increased because that the symmetry in N-Ag vibration was be enhanced due to the proportion of Ag-PHZ in complex $(AgBTA)_{1-x}/(Ag\text{-}PHZ)_x$ increased. It also led to the IR spectrum of AgBTA after treated with PHZ solutions were more and more similar to that of Ag-PHZ in higher wavenumber side.

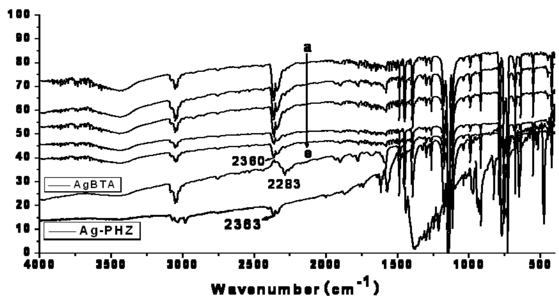

Figure 2. IR spectrum of AgBTA grains treated with PHZ solutions. Ratio of AgBTA and PHZ (mol:mol). a.1:0.1; b.1:0.2; c.1:0.5; d.1:0.7; e.1:1

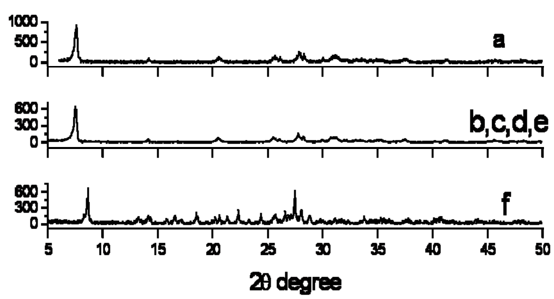

***Figure 3**. XRD data of AgBTA grains treated with PHZ solutions. Ratio of AgBTA and PHZ (mol:mol). a.AgBTA; b.1:0.2; c.1:0.5; d. 1:0.7; e.1:1; f. Ag-PHZ*

The XRD data of AgBTA grains after treated with PHZ solutions were shown in figure 3. As results of x-diffractometer, the peaks of complex were at the same position but weaker compared with original AgBTA. The peaks intensities of complex decreased due to the amount of AgBTA in complex $(AgBTA)_{1-x}/(Ag\text{-}PHZ)_x$ were smaller than that of original AgBTA. Ag-PHZ was formed in complex led to the proportion of AgBTA in complex decreased. There were no new peaks appeared in XRD spectrum of complex. This result showed that the complex had the same crystal structure as AgBTA and Ag-PHZ in complex was no-fixed structure.

Conclusions

The results indicated that H_2PA as a toner could improve the development in high pH of system and the development promotion increased with the increasing amount of H_2PA during thermo-imaging process in PTG materials based on silver benzotriazole as silver source. We also found that the development of silver benzotriazole materials was promoted by the introduction of PHZ, and the promotion was strengthened by increasing the amounts of PHZ. The analysis data of SEM and IR indicated that a silver complex, which was supposed to be easy to transmit silver ions to development center to promote development, have been produced by introducing PHZ into the silver benzotriazole materials. The shape of silver benzotriazole grains were changed by the silver complexes. The XRD data showed that the silver complexes had the same crystal structures as silver benzotriazole.

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Author Biography

Shi Yao received her Bachelor of Engineering in fine chemistry from East China University of Science and Technology in 1996, and MS, PhD degrees in physical chemistry from Technical Institute of Physics and Chemistry of CAS in 2004 and 2008 respectively. Since 1996 she has been working at Technical Institute of Physics and Chemistry of CAS. Her works focus on researching and developing special radiography films and photothermographic imaging materials.