Effect of Nicotinic Acid as a Toner on Photothermographic Materials Based on Silver Benzotriazole

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Abstract

The photothermographic(PTG) imaging materials are the kind of digital hardcopy imaging medium usually used in diagnostic medical field. The hardcopy image was obtained by thermal printing process using driving laser or thermal print head on PTG materials based on electronic data. Toner, as the most important of components to provide better image quality, is a compound could modify the shape and size of Ag_0 particles to correct the image color from yellow-brown to black in thermal imaging process. In the paper, the effect of nicotinic acid as a new toner on PTG based on silver benzotriazole as silver sources had been studied. The results indicated that development of silver benzotriazole PTG materials was promoted by the introduction of nicotinic acid and the function of nicotinic acid was influenced by the pH of the silver benzotriazole emulsion and the amounts of nicotinic acid. The promotion of nicotinic acid was strengthened with the pH in system increased in the condition of the same amounts of nicotinic acid added in PTG emulsion. The best promotion could be obtained in the case of the mol ratio of nicotinic acid to silver benzotriazole 0.1 and value of pH in emulsion about eight. The IR spectrum data implied that the silver complex, which was supposed to be easy to transmit silver ions from silver salt to development center, was produced by nicotinic acid and 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. As the chemical roles of the toners have become clearer, it is probably more appropriate to call toners development accelerators or promoters.

The most popular toners are phthalic acid(H_2PA) and phthalazine(PHZ) in PTG imaging materials. Many research results shown that H_2PA was the silver ion carrier during thermo-imaging process in PTG system based on silver behenate as silver sources[2] and silver complex produced by H_2PA and silver salt not only improve silver salt solubility but also change its redox potential in thermal imaging process[3]. The study on PHZ suggested 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]. 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 [5]. And PHZ/H_2PA toner system which was used widely has the best effect in PTG imaging materials. 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.

All toners reported in literature include an aromatic nitrogen or a nitrogen which can combine with metal silver ion. This structure in the toners has provided the basis for the proposal that the role of these compounds is to transport silver ion to the reduction imaging centers[6]. H_2PA is an aromatic organic acid and PHZ is an aromatic nitrogenous heterocyclic compounds. Silver complex which can move to carry silver ion were created by H_2PA, PHZ and silver salt during thermo-imaging process. In the structure of silver complex, silver ion were combined with heterocyclic nitrogen atom in PHZ and carboxylic oxygen atom in H_2PA[5]. According to mechanism of PHZ/H_2PA toner system, the PHZ/H_2PA toner system might be replaced by an aromatic nitrogenous heterocyclic compound with carboxyl substituent as a toner. The nicotinic acid（3-pyridinecarboxylic acid）as a new toner was used to study its toning effect on photothermographic materials based on silver benzotriazole as silver sources in this paper.

Experimental

Silver benzotriazole (AgBTA) were prepared by the method in reference 7.

The PTG emulsion were mixed with AgBTA(silver benzotriazole) as silver sources, NH_4Br as halogenating agents to form AgBr as photocatalysts, nicotinic acid as toner, PVA(polyvinyl alcohol) as binders and pyrogallic acid as 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 after drying.

The silver benzotriazole after treated with nicotinic acid solutions were investigated by Fourier transform infrared spectrophotometer.

Results and Discussion

1. Effect of nicotinic acid on PTG system based on silver benzotriazole

The effect of nicotinic acid as a toner on PTG system based on silver benzotriazole as silver sources were shown in Table 1, 2 and 3. The development minimum density(D_0) of samples were almost same and Development maximum density(D_{max}) were increased firstly then decreased with increasing the amount of nicotinic acid in table 1. D_{max} was top value when the amount of nicotinic acid was 10%. The results shown that nicotinic acid as a new toner can improve development and its promotion was affected by the amounts of nicotinic acid added in system. The development was promoted because that these silver complexes created by nicotinic acid and silver banzotriazole might transfer silver ion from silver salt to imaging center to improve development. The D_{max} was reduced because of acidity of nicotinic acid, similar as phthalic acid(H_2PA)[7]. In the condition of nicotinic acid used in system from 1.0% to 10%, the capability of nicotinic acid combined with organic silver salt to transport silver ion was main effect compared with acidity of nicotinic acid. So the D_{max} were enhanced with nicotinic acid increased because of the silver complex created more. In the condition of amount of nicotinic acid from 15% to 20%, the acidity of nicotinic acid was main factor so that the development density was reduced by nicotinic acid increased.

Table 1. The influence of nicotinic acid on photothermographic imaging materials

nicotinic acid (mol/100mol AgBTA)	pH	Minimum density (D_0)	Maximum density (D_{max})
0	7.72	0.50	0.67
1.0	7.52	0.56	0.78
2.5	6.52	0.53	0.93
5.0	5.70	0.51	0.95
7.5	5.32	0.50	1.01
10	5.04	0.50	1.18
15	4.74	0.56	0.84
20	4.53	0.58	0.68

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

nicotinic acid (mol/100mol AgBTA)	pH	Minimum density (D_0)	Maximum density (D_{max})
0	7.98	0.44	0.68
1.0	8.03	0.59	0.82
2.5	7.94	0.60	0.88
5.0	8.01	0.66	0.93
7.5	8.01	0.58	1.08
10	8.05	0.55	1.35
15	8.07	0.61	1.39
20	8.07	0.69	1.43

In table 2, the results indicated that D_0 were increased very slowly, and D_{max} were enhanced obviously with the amount of nicotinic acid increased when pH in system were almost same at about 8. On this approximate pH about 8, the capability of nicotinic acid combined with organic silver salt to transport silver ion was main effect. The more silver complexes were created by nicotinic acid 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 (D_{max}) when the amount of nicotinic acid added into system were increased.

An interesting phenomenon was also showed in table 1 and table 2 that developing densities of sample were promoted selectively by nicotinic acid. In unexposure area of sample, silver clusters as imaging catalysis centers were almost not formed by AgBr absorbed light quanta. The promotion of nicotinic acid was little effect when the imaging catalysis centers were formed seldom. So the D_0, development densities of unexposure region of samples, were almost same. In exposure area, the toning function were visible with imaging center existed conversely so that D_{max}, densities of exposure region of samples, were enhanced. This result suggested that nicotinic acid as a new effective toner could be useful for getting good image quality.

Table 3. The influence of pH in system on photothermographic imaging materials (the amount of nicotinic acid was 10%)

nicotinic acid (mol/100mol AgBTA)	pH	Minimum density (D_0)	Maximum density (D_{max})
10	5.04	0.50	1.18
10	6.05	0.51	1.21
10	7.06	0.55	1.27
10	8.05	0.55	1.35
10	9.06	0.85	1.40
10	10.05	1.20	1.46

The results of table 3 shown that the development densities including D_0 and D_{max} were all enhanced very slowly in acidic range (5~7) with the pH in system increased. The density D_0 were increased quickly and D_{max} were raised laxly in basic range (8~10). In acidic range, the capability of nicotinic acid combined with organic silver salt to transport silver ion were affected faintly by pH of system so that densities were not increased observably. On the other way, developer, pyrogallic acid, as an organic acid compound was less active in acidic range also led to the densities was increased slowly. However, the combination of nicotinic acid and silver salt was promoted with the pH increased in basic system. The silver complexes which improve development were introduced more so that densities D_{max} were bigger. Otherwise, the developing properties of developer were more active in basic range. The silver salt could be reduced directly by developer without imaging catalysis center on high pH (~10) especially. So it led to D_0, development density of unexposure region of sample, was increased obviously.

Comparing data of table1, table 2 and table 3, we found that nicotinic acid as a new effective toner can promote development and the toning function of nicotinic acid was influenced by the pH of the silver benzotriazole emulsion and the amounts of nicotinic acid. The promotion of nicotinic acid was strengthened with the pH in system increased in the condition of the same amounts of nicotinic acid added in PTG emulsion. The best toning effect was obtained in condition of the amount of nicotinic acid was 10% and the value of pH in system was eight.

2. Mechanism of nicotinic acid as a toner in PTG system based on silver benzotriazole

The IR spectrum of AgBTA grains after treated with nicotinic acid solution was shown in figure 1. 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 nicotinic acid 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 nicotinic acid and silver ion just like the data of PHZ in our previous paper[8]. The IR spectrum implied that a new complex which transfer silver ion to promote development might be formed after AgBTA treated with nicotinic acid solutions.

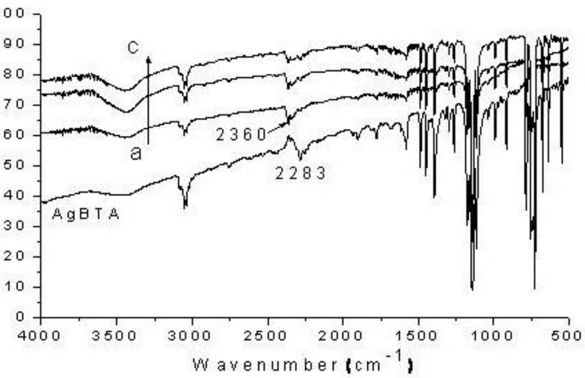

***Figure 1**. IR spectrum of AgBTA grains treated with nicotinic acid solutions. Ratio of AgBTA and nicotinic acid (mol:mol). a.1:0.05; b.1:0.1; c.1:0.2*

Conclusions

The results indicated that nicotinic acid as a new effective toner could improve the development in PTG system based on silver banzotriazole as silver sources. The toning function of nicotinic acid was affected by the pH of the silver benzotriazole emulsion and the amounts of nicotinic acid. The promotion of nicotinic acid was strengthened with the pH in system increased in the condition of the same amounts of nicotinic acid added in PTG emulsion. The best toning effect of nicotinic acid could be obtained in the case of the mol ratio of nicotinic acid to silver benzotriazole 0.1 and value of pH in emulsion about eight. The IR spectrum data implied that the silver complex, which was supposed to be easy to transmit silver ions from silver salt to development center, was produced by nicotinic acid and silver benzotriazole.

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Author Biography

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