

The Reaction Mechanism of Thermally Developed Photographic System Based on Silver Carboxylate

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Abstract

The reaction mechanism of thermally developed photographic system based on silver carboxylate has been investigated both in the model system and in the film sample. The reaction path has been found to consist of the following steps:

- (1) Disintegration of crystal structure of silver carboxylate under thermal development,
- (2) Formation of silver-ion carriers, which can diffuse in the molten media,

and

- (3) Reduction of silver ion to metallic silver by the reducing agent.

In the step (2), the structures of silver-ion carriers have been determined by using ^{13}C -NMR, density functional calculation of ^{13}C -NMR chemical shift, and TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry). The diffusion coefficient of silver-ion carriers has been measured by pulsed-field-gradient ^1H -NMR at the development temperature. As a result, the complexes of phthalazine and silver-ion are the silver-ion carriers in molten media. In the step (3), the reduction reaction of silver ion by the bisphenol-type reducing agent has been analyzed by the identification of the reaction products using HPLC and LC/MS. It has been found that this reducing agent has eight-equivalent reducing power. The reaction mechanism of thermally developed photographic system based on silver carboxylate has been proposed.

Introduction

On the thermally developed photographic system consisting of silver halide, silver carboxylate, and the developer dispersed in the binder, the reaction mechanism has been reported by a lot of workers. For example, Bokhonov and co-workers have investigated the morphology of silver grains formed during thermal development.¹ Geuens has studied the thermal behavior of

silver behenate crystal using XRD.² Whitcomb *et al.* have carried out the crystal structural investigation and have reported the silver complexes including phthalazine, phthalic acid and silver ion.³⁻⁵ Klosterboer and Hirano have built mathematical models to simulate the thermal reaction.⁶⁻⁷ Klosterboer *et al.* have observed the thermal development process in the film by TEM and have noted that the silver behenate around the developed silver has disappeared. They have called this area as "spheres of influence" and this phenomenon has been also observed in our sample (the white area in Photo. 1). The size of this spheres of influence grew larger as the thermal development proceeds. Therefore we think that the silver ion dissolves and diffuses in the molten carboxylic acid and is then reduced by the developing agent near the developed silver. It should be noted that the detail of the diffusion process and the reduction reaction of silver ion has not been clarified yet. The goal of our study is to determine the structure of silver-ion carrier, to evaluate its diffusion coefficient, and to view the reaction mechanism of the reduction of silver ion by the reducing agent.

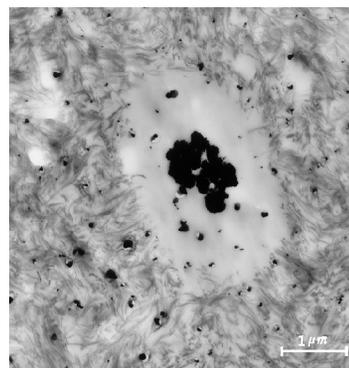


Photo. 1. Ultra-thin Section of the Thermally Developed Photographic film observed by TEM.

Experimental

For the thermal development, the co-existence of four species such as silver behenate, phthalic acid, phthalazine, and reducing agent, was necessary in the film sample. The heat treatment of the powder mixtures of those four species resulted in the formation of metallic silver, too. Therefore, we used the powder mixtures of these four species as the simplified model.

The powder samples were mixed with behenic acid and heated at 393 K. To check the solubility in the molten-state behenic acid, $^1\text{H-NMR}$ measurement was performed using 400 MHz NMR (Bruker DPX-400). The long-range periodic structure of silver behenate was evaluated by X-ray diffractometers (Rigaku RINT-2000).

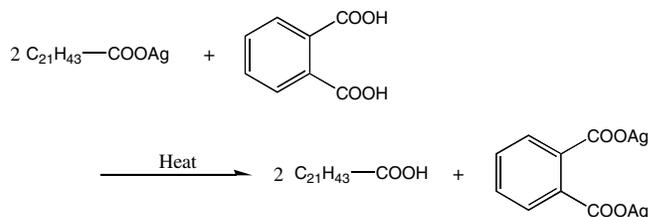
To identify the structures of thermal reaction products, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and $^{13}\text{C-NMR}$ were used. In the TOF-SIMS measurement, the samples were embedded in the Indium plate and then introduced to the analytical chamber. The TOF-SIMS spectra were obtained using Physical Electronics TRIFT-II instrument equipped with a 15 kV $^{69}\text{Ga}^+$ primary beam with 10 ns pulse width. The sample charge up was compensated by the electron beam, which was pulsed between periods of secondary ion collection. The positive and negative secondary ions with mass peaks up to m/z 1000 were collected. $^{13}\text{C-NMR}$ measurements were done in a similar manner as $^1\text{H-NMR}$ measurements.

The diffusion coefficients of silver-ion carriers have been determined by pulsed-field-gradient $^1\text{H-NMR}$ measurement at the development temperature. The PFG measurements were performed by using the inverse BB probe equipped with the PFG coil (Great 1/10, Bruker).

Results and Discussion

Formation of silver phthalate

It is found that the X-ray diffraction peaks of silver behenate disappear when powders are mixed with phthalic acid and are heated at 393 K. Instead, the new diffraction peaks appear at $2\theta = 5.3, 10.1,$ and 16.4° . These peaks coincide with those of behenic acid. FT-IR measurements of those mixed powders show that the peak at 1520 cm^{-1} decreases and new peak at 1560 cm^{-1} increases after heating at 393 K. The IR peaks at 1520 cm^{-1} and 1560 cm^{-1} are assigned to carbonyl (CO) stretching vibrations of silver behenate and of silver phthalate, respectively. In contrast, no change in the X-ray diffraction pattern is observed when silver behenate is mixed with phthalazine. It is strongly suggested that phthalic acid receives silver ion from crystalline silver behenate and becomes silver phthalate. This is the first reaction process [step (1)] in the thermal development.



Identification of silver ions carrier

$^1\text{H-NMR}$ signals of silver phthalate are not observed in the mixture of silver phthalate and behenic acid at 393 K. This simple experiment clearly shows that silver phthalate does not dissolve in the molten behenic acid and can not diffuse fast in this media. Thus, silver phthalate, formed at the first step of thermal development, is not a silver-ion carrier.

Figure 1 shows the high-resolution TOF-SIMS spectra (positive) of silver phthalate in the presence of phthalazine and behenic acid after heating at 393 K. The MS spectrum including peaks at m/z 236.97 and m/z 238.96 is assigned to the complex of silver (^{107}Ag and ^{109}Ag) ion and phthalazine with 1:1 ratio. Similarly, a set of peaks at m/z 367.02 and m/z 369.01 is identified as the 1:2 ratio complex of silver ion and phthalazine.

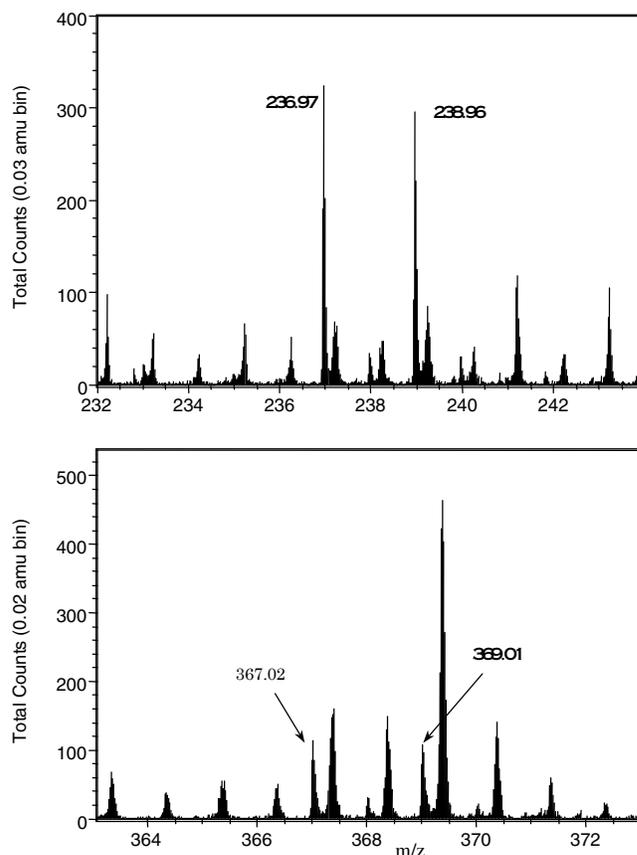
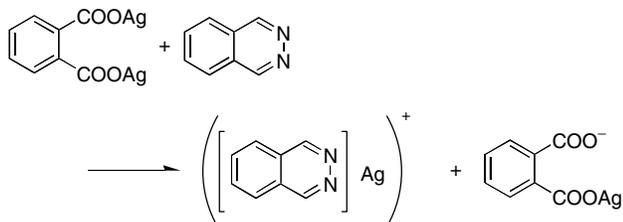


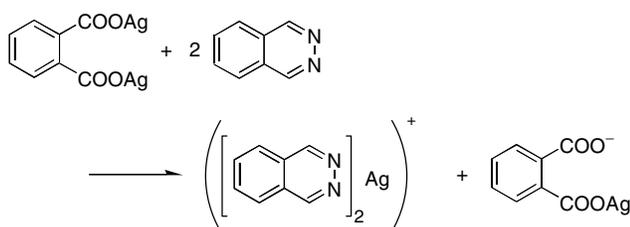
Figure 1. TOF-SIMS spectra of silver ion carriers.

^{13}C -NMR spectrum of silver phthalate and phthalazine mixture is measured in molten behenic acid at 393K. The chemical shift of carbon atom adjacent to nitrogen atom in phthalazine (alias as C*N) with silver ion is observed at 151 ppm, a 2-ppm low field shift compared to that of phthalazine. The density functional calculation shows that the chemical shift of C*N shows a 3-ppm low field shift. The coordination of silver ion to the nitrogen atom of phthalazine is estimated by ^{13}C -NMR method.

for the complex of silver ion and phthalazine with 1:1 ratio



for the complex of silver ion and phthalazine with 1:2 ratio



Diffusion coefficient of silver ion carrier

Silver phthalate and phthalazine are mixed with behenic acid and are heated at 393 K. ^1H -NMR peaks at 7.6, 7.8, and 9.4 ppm are assigned to silver-phthalazine complexes. The diffusion coefficients of silver-phthalazine complexes in the molten behenic acid are measured by PFG-NMR. The observed diffusion coefficient, $D = 5.6 \times 10^{-6} \text{ cm}^2/\text{s}$, is smaller than that of phthalazine ($D = 7.1 \times 10^{-6} \text{ cm}^2/\text{s}$). Diffusion coefficients of phthalazine, phthalic acid, and bisphenol are evaluated by PFG-NMR in the molten behenic acid. The molecular volumes of these compounds are calculated at the HF/3-21G level. The calculated volumes and the diffusion coefficients satisfy Einstein-Stokes equation (1),

$$D = RT/6\pi N\eta a \quad (1)$$

where R is a gas constant, T ; the absolute temperature, N ; the Avogadro number, η ; the viscosity, and a is the radius of the particles. It is suggested that the diffusibility of silver-phthalazine complexes in the molten behenic acid are in the same order as that of compounds dissolved in the solvent at room temperature. Thus, silver-phthalazine complexes have the ability to carry the silver ion fast at the development temperature.

Reaction mechanism of reducing agent

We prepare model films consisting of silver behenate, phthalic acid, phthalazine, bisphenol-type reducing agent and silver bromide grains. The film is exposed and thermally developed. The reaction products in the film are extracted and analyzed by using LC/MS method. Five species are identified and these are two-electron oxidation products of the reducing agent, two types of four-electron oxidant, six-electron oxidant and eight-electron oxidant, respectively. Figure 2 represents the amounts of each product measured by HPLC during thermal development. At the initial stage of thermal development, the amount of reducing agent decreases rapidly, followed by increasing two-electron oxidant. And then, the decrease of two-electron oxidant and the increase of four-electron oxidant are observed. At the end of the development, six-electron and eight-electron oxidants are the main products. The consecutive reactions of the reducing reagent occur during the thermal development. The recovery of these five reaction products ranges from 70 to 90 %. It is estimated that the consecutive reactions are the main reaction in the film.

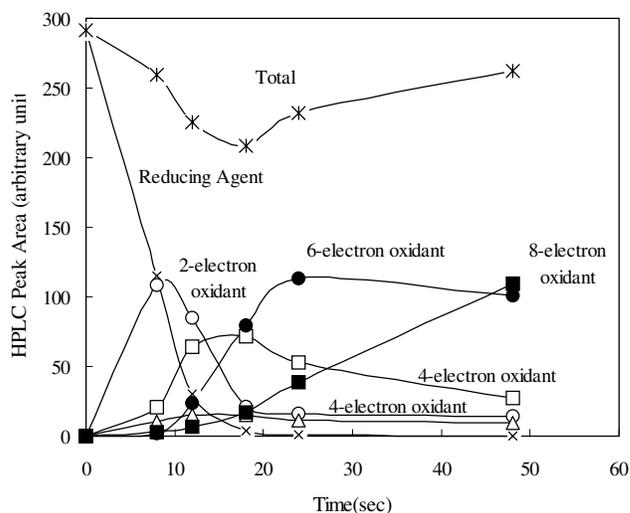


Figure 2. Reaction Products in the film after thermal development.

Conclusion

The structures of silver-ion carriers are clarified by ^1H , ^{13}C -NMR and TOF-SIMS methods. Silver-ion carriers dissolve in the molten behenic acid and its mobility reaches in the order of $10^{-6} \text{ cm}^2/\text{s}$. The reaction mechanism of the reducing agent is estimated by analyzing the reaction products in the film. The view of reaction scheme is proposed by both experimental and theoretical approaches.

References

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Biography

Toshihiko Maekawa received his master's degree in Polymer Chemistry from Waseda University at Tokyo in 1985. The same year and since then, he has worked in Ashigara Research Laboratories at Fuji Photo Film Co., Ltd. He has been engaged in the research of analytical chemistry.