Study of Sulfide Solutions as Inkjet Inks for Color-changeable Ag Films

Shuichi Maeda[1,2], Taito Sugiura[1], Yohei Ito[1]; [1]Optical and Imaging Science & Technology, Faculty of Engineering, Tokai University, Kanagawa/Japan, [2]Course of Electro Photo Optics, Graduate School of Engineering, Tokai University, Kanagawa/Japan

Abstract

We have recently discovered a novel and easy method for preparing color-changeable Ag films using aqueous solutions of sulfides as coloring agents. In the presence of specific sulfides such as lime sulfur solutions, the color of Ag films, initially sliver, changes to yellow, red, blue and green depending on the preparation conditions such as the dipping time in the solutions and the temperature of the solution. One of the potential candidates is in the application as imaging materials. Assuming the imaging by inkjet devices, we have already investigated the ink receiving nature to Ag films. The focus of this present work is to explore the nature of sulfide solutions which act as inks for changing the color of Ag films in the inkjet system. We found that both the solubility of sulfides in water and the nature of the hydrolyzed constituents of sulfides are important parameters for obtaining successful color-changeable Ag films in this imaging system. For example, K_2S solution works well as coloring agent due to its appropriate solubility in water and KSH, one of the hydrolyzed constituents of K_2S, play an important role to change the color of Ag films.

1. Introduction

It is generally known that Ag films are easily sulfurized in the presence of sulfide and turn their silver surfaces to spotted black ones (see Figure 1(b)). This is generally undesirable because the changeable color is limited to black and the color leads Ag films to lose the gloss on their surfaces. By contrast we have discovered a novel method for preparing Ag films which have various colors with keeping their glosses as shown in Figure 1 (c), (d) and (e). In this method, Ag films made by sliver mirror reaction are colored by dipping them in specific aqueous solutions of sulfides. The color of the films, initially silver changes to yellow, red, and blue.

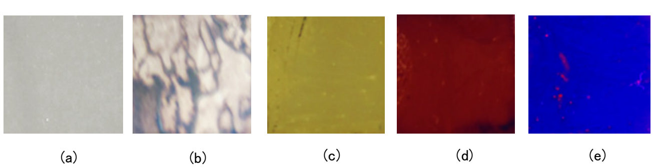


***Figure 1**. Ag films; (a) made by silver mirror reaction, (b) dipped 30 sec in a 1.0 w/w%, 50°C Na_2S solution, (c)-(e) dipped 15, 45, 90 sec respectively in a 1.0 w/w%, 40 °C aqueous solution of lime sulfur solution which is the mixture of CaS and CaS_5*

It is of great industrial interest how to control the color of the Ag films. Therefore, in the previous works [1]-[14], we firstly focus on the relationship between the preparation conditions and the resulting colors of Ag films [1]-[4]. It is also of great scientific interest to elucidate the mechanism of the color change of the Ag films. In order to address the mechanism, these Ag films have been characterized in terms of their surface morphology and particle size by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy [5]-[7].

These color-changeable Ag films have a number of potential applications including coating materials, imaging materials, and optical memories, since the film is easy to prepare, low cost, and applicable to a large area [8]-[11]. One of promising candidates is in the application as imaging materials. Considering the industrial application, it is preferable to give an ink receiving nature to Ag films, assuming the imaging by inkjet devices. Therefore, we explored the potential for the Ag films as inkjet imaging media using an electrostatic inkjet device as shown in Figure 2 and obtained inkjet images on the Ag films as shown in Figure 3 using an aqueous solution of lime sulfur as the ink [12]-[14].

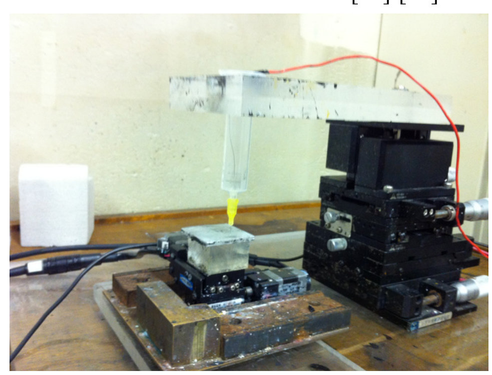


***Figure 2**. Electrostatic inkjet device for imaging on Ag films with sulfide solutions as inks*

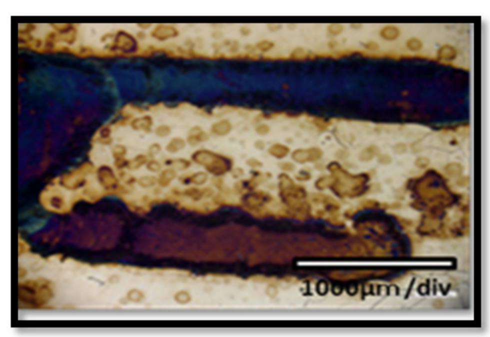


***Figure 3**. Inkjet imaging on a Ag film using a 1.0 w/w%, 60 ℃ aqueous solution of a lime sulfur as the ink*

We have intensively investigated the nature of the color-changeable Ag films as mentioned above, with particular emphasis the mechanism of color changes. Our scanning electron micrographs show that the surface particle size of the non-colored Ag film has particulate dimensions in the range of 10-30 nm. On the other hand, the surface particle size of the purple-colored Ag film in the presence of a lime sulfur solution is larger than the dimensions of the non-colored one and the range is in 60-100 nm. Therefore, we first thought that the particle size play an important role in the color change of the Ag films. Thus with regard to the color change of Ag films, the surface plasmon resonance due to the particle size change of surface Ag nanoparticles was considered as one of the driving forces of the coloration [5].

However, it is generally known that surface plasmon resonance can be observed in not bulk but isolated nanoparticles. Therefore, we also reported another mechanism for the color change of Ag films [6]. In this report, our XPS depth analyses data suggest that the blue-colored Ag film dipped in potassium sulfide solution contains sulfur to the depth of at least 30 sec sputtering time and the sulfur has gone at the depth of over 40 sec sputtering time. It is possible to think that the sputtering time corresponds to a Ag_2S layer. In other words, we think that there is a Ag_2S layer on the Ag film. As the results, at present, we conclude that the color change of our Ag films comes from not surface plasmon resonance of due to the particle size change of the Ag nanoparticles but the thin film inference between Ag and Ag_2S layers.

We also think that another important factor for obtaining successful colored Ag films is the sulfide solutions which act as inks for changing the color of Ag films in the IJ system. Therefore, the focus of this present paper is concerned with the nature of sulfide solutions which act as inks for the color-changeable Ag films. We elucidate what kinds of the chemical constituents in sulfide solutions are effective to change the color of Ag films in the inkjet systems.

2. Experiment

In order to investigate the effects of sulfide solutions as the coloring agent to Ag films, we carried out a simple dipping test instead of an imaging test by IJ printing systems.

Ag films prior to the color treatment were made on ca. 10 x 10 mm plastic boards by sliver mirror reaction using two head spry as shown in Figure 4 as described elsewhere [8]-[9].

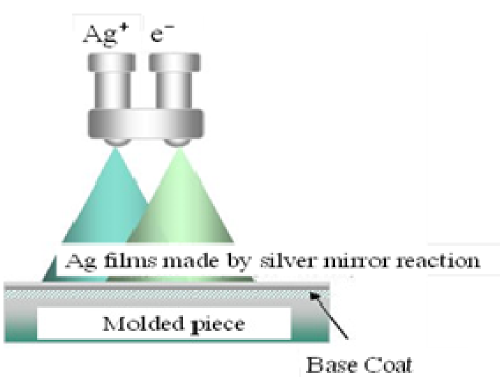


Figure 4. Schematic diagram showing two head spry method for obtaining Ag films by silver mirror reaction

Typical procedures for coloring Ag films by sulfide solutions were carried out as follows: 4 pieces of Ag films on plastic board to tips of chopsticks were dipped in a 50 ml of a 1.0 w/w%, 50 °C aqueous solution of potassium sulfide (K_2S, Wako Pure Chemical Industries, Ltd.) as shown in Figure 5. The dipping was allowed to 5, 10, 15, and 20 sec.

The pieces were then picked up, rinsed by de-ionized water, and dried in air. Essentially the same procedures were repeated using other sulfide solutions. These sulfides include sodium sulfide (Na_2S), barium sulfide (BaS), and calcium sulfide (CaS). In addition, the same procedures were repeated using the sulfide hydrolysates such as KSH, KOH, NaSH, and NaOH.

The solubilities of these sulfides are experimentally measured in 100 g of water at 50 °C.

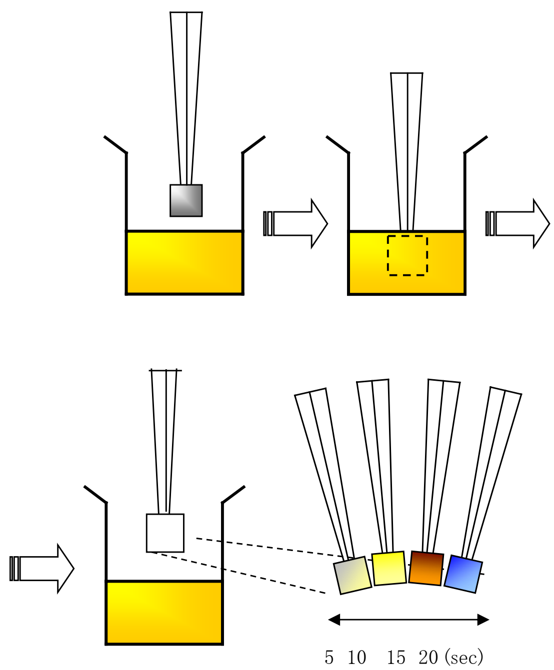
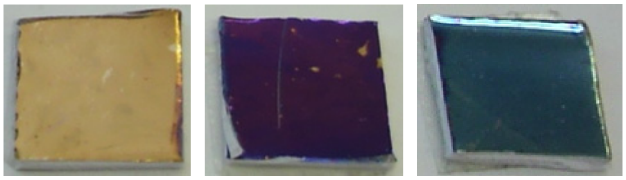


Figure 5. Schematic diagram showing the coloration of Ag films dipped in a 50 ml of a 1.0 w/w%, 50 °C aqueous solution of potassium sulfide (K_2S)

3. Results and Discussion

Ag films dipped in K_2S solution are shown in Figure 6 with their preparation conditions. The surface of the Ag films dipped in K_2S solution turned yellow, purple, and blue respectively. The color images of Ag films dipped in K_2S solution are similar those in dipped in lime sulfur solution presented in Figure 1 (b), (c) and (d). In this preparation, we obtained different colors of Ag films as a function of the dipping time in a K_2S solution. This result suggests that we can control the colors of Ag films by changing only the dipping time in K_2S solution.

However, in the actual application in the IJ system, we have to control the concentration and temperature of K_2S solution as the ink because we can't the dipping time in IJ systems. Although not mentioned in detail here, we have already found that the there is a correlation between the concentration and/or temperature of the K_2S solution and the color change of Ag films.



(a) (b) (c)

***Figure 6**. Ag films dipped (a) 5, (b) 10, (c) 20 sec in a 1.0 w/w%, 50 °C aqueous solution of K_2S*

On the other hand, in the presence of Na_2S solution, the Ag films were partially changed to black. They seem to be the same to undesirable spotted black when silver jewelries are sulfurized.

By contrast, in the case of BaS and CaS, no color change of Ag films were observed as shown in Figure 7 under any preparation conditions.

***Figure 7**. Ag films dipped 10 sec in a 1.0 w/w%, 50 °C aqueous solution of Na_2S*

(a) (b)

***Figure 8**. Ag films dipped 50 sec in a 1.0 w/w%, 50 °C aqueous solution of (a) Bas and (b) CaS*

A summary of the experimental data showing the relationship between the solubility of sulfides and the resulting colors of the Ag films are presented in Table 1. We found that the solubility sulfides are related to the color change of Ag films. In the case of Na_2S which has the highest solubility here, probably the sulfurizing power is too strong to control the color of the Ag films. By contrast, insoluble BaS and CaS may not have any power to change the color of Ag films at all. Only K_2S seems to have the appropriate solubility for obtaining various colors on the Ag films. It is still unclear at present whether the solubility of sulfides is the only parameter for changing the color of Ag films. However, it can be said that controlling the solubility of sulfides is at least one of the key technologies in obtaining successful color changes of Ag films.

Table 1. Summary showing the relationship between the solubility of sulfides and the resulting colors of Ag films

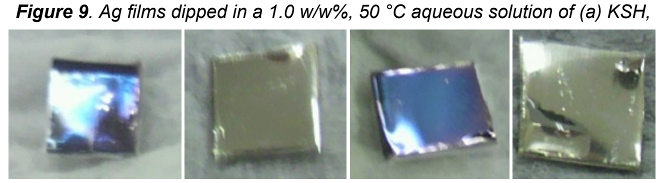
Sulfide		Preparation Condition		Result	
Constituent	Solubility In 100g H_2O At 50 °C (g)	Temp. (°C)	Dipping Time (sec)	Color change	Color image
K_2S	8.7	50	20	Yes	
Na_2S	15.2	50	10	partially	
BaS	0	50	50	No	
CaS	0	50	50	No	

It is well known that both K_2S and Na_2S are hydrolyzed as follows.

$$K_2S + H_2O \rightarrow KSH + KOH$$
$$Na_2S + H_2O \rightarrow NaSH + KOH$$

It is interesting to identify which chemical constituent actually play important roles for the color change of Ag films. We found that KSH and NaSH work as coloring agents for Ag films as shown in Figure 9 (a) and (c), while KOH and NaOH don't as shown in Figure 9 (b) and (d). Therefore both KSH and NaSH can be utilized as inks for changing the color of Ag films instead of K_2S.

***Figure 9**. Ag films dipped in a 1.0 w/w%, 50 °C aqueous solution of (a) KSH,*



(a) (b) (c) (d)

(b) KOH, (c) NaSH, and (d) NaOH

4. Summary

It can be summarized that the key technology in obtaining successful color change of Ag films using IJ system is to find appropriate sulfide solutions as the inks which have appropriate solubilities. In addition, we identified that the sulfide hydrolysates such as KSH and NaSH play important roles for the color change of Ag films.

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Author Biography

Shuichi Maeda is a professor of Optical and Imaging science & technology at Tokai University. He received his M.Eng. and Ph.D. in polymer chemistry from Keio University and Sussex University, respectively. He used to work for the research laboratory at Oji paper company. In 2010, he moved to Tokai University. His current interests are imaging materials, security technology and electronic paper.

Taito Sugiura is expected to receive his B.E. degree in 2014 from Tokai University. He is now engaged in a study of organic conducting polymer inks.

Yohei Ito is expected to receive his B.E. degree in 2014 from Tokai University. He is now engaged in a study of mechanism of color-changeable Ag film with sulfides.