Chemical Roles of Gelatin in Photographic Emulsions — Silver Cluster Formation and Stabilization —

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Abstract Chemical roles of gelatin in AgBr emulsions were studied in relation to their stabilization. Ionic conductivity of AgBr grains and ultraviolet photoelectron spectra (UPS) of AgBr layers revealed that stabilizers such as TAI (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) could work by influencing the properties of AgBr grains only in the presence of gelatin. It was confirmed from the measurements of sensitometry, electrochemistry, and UPS that silver clusters as assigned to reduction sensitization centers were formed owing to the reduction of silver ions by gelatin during precipitation of AgBr grains, digestion of liquid emulsions, and storage of dried emulsion layers. One of the causes for the destabilization of AgBr emulsions was therefore the reduction of silver ions by gelatin, and was depressed by stabilizers forming scarcely soluble silver salts.

Key words: gelatin, stabilization, reduction sensitization, emulsion, silver halide

Introduction

This paper is based on the keynote lecture of the session on Advanced Science and Technology of Gelatin for Imaging in ICIS'02, the 29th International Congress of Imaging Science on May 13-17, 2002 in Tokyo 1). The lecture was arranged to meet the requirements of the session co-chairpersons that it should be given from the viewpoint of emulsion technology.

Gelatin is an irreplaceable binder for silver halide photographic materials, and play important roles in physical and chemical aspects of photographic phenomena 2). Physical roles include its activities to act as a protective colloid for silver halide grains and to control the nucleation and growth of the grains. Chemical roles include its activities to control dissociation and adsorption of chemical species to silver halide grains and to form Ag clusters by reducing silver ions on the surface of silver halide grains. Although the knowledge of the physical roles is very important for emulsion technology, it is rather delicate and is too confusing to be systematically analyzed and described at the present. Thus, this paper is focused on chemical roles of gelatin in emulsion technology.

Although the activities of gelatin to control dissociation and adsorption of chemical species to silver halide grains have not necessarily attracted keen interests of photographic scientists, reducing activity of gelatin has been extensively studied for many years by many photographic scientists. There are many literatures describing the origins of reducing power of gelatin, which included mechinone, sulfite, aldehydes, and reducing sugars 3). Steigman proposed mechinone as the origin of reducing power of gelatin as early as in 1950 4). Recently, reducing sugars in gelatin have been extensively studied by H. Kobayashi et al. 5) and S. and Takehiro Tani 6). As to the origin of reducing power of gelatin, this paper entirely depends on the above-stated literatures.

There are many literatures describing evaluation methods of reducing power of gelatin, which included redox titration as proposed by S. Kikuchi et al. as early as in 1947 7), surface plasmon absorption of Ag clusters 8) formed by Vogel reaction 9), redox potential as proposed by J. Pouradier 10), and comparison of gelatin with synthetic polymers by Urabe and Sano 8). In this paper, the reducing power of gelatin in its aqueous solution was evaluated by the difference in redox potential between silver and gelatin half-cells. The reducing power of gelatin in dried emulsion layers, which could not be evaluated by electrochemical potentials, was evaluated by the difference in Fermi level between gelatin and silver halide in the view of its equalization, according to which an electron should move from phase with higher Fermi level to that with lower Fermi level until the Fermi levels would be equalized between them. It is noted that the redox potential of a solution corresponds to the Fermi level of a solid.

There are also many literatures describing photographic effects of reducing power of gelatin 2) 8) 11-24), which included reduction of Au (III) ions 11), reaction with photolytic halogen as halogen acceptor 15), and formation of silver clusters during precipitation and digestion of silver halide emulsions. 12) 14) 15) 17-24). This paper deals with the formation of reduction sensitization centers during precipitation and digestion of liquid AgBr emulsions, and storage of dried AgBr emulsion layers. A discussion will be made on the mechanism of stabilization of AgBr emulsions on the basis of the above-stated experiments.

Adsorption of Stabilizers to AgBr

Among many stabilizers and antifoggants, TAI (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene), BT (benzotriazole), PMT (1-phenyl-2-mercaptotetrazole), and KSCN are popular 2) and subjected to the study of their behavior on AgBr in this paper.

It is known that silver ions at kink sites on the surface of AgBr are unstable, and that many of them jump into interstitial positions to form positive space charge layer with negative charges on the surface and positive charges with interstitial silver ions in
the interior \(^2\)). In this space charge layer, the electronic energy levels such as the top of the valence band and the bottom of the conduction band are therefore higher on the surface than in the bulk. It is also known that anions of the above-stated compounds bring about photographic effects by combining with (i.e., stabilizing) silver ions on the surface of silver halides \(^2\). It is therefore expected that anions of the above-stated compounds depress the above-stated space charge layer by decreasing the concentration of interstitial silver ions in AgBr.

It was confirmed in the former paper \(^25\) that the above-stated compounds decreased the concentration of interstitial silver ions, bringing about the decrease in the difference in potential by as large as 0.1V between the surface and bulk of cubic AgBr grains with edge length of 0.2\(\mu\)m. It was therefore expected that the above-stated compounds decreased the height of the top of the valence band on the surface of AgBr with respect to that in the bulk by as large as 0.1eV.

The height of the top of the valence band of an AgBr layer in the presence and absence of a thin gelatin membrane was measured with respect to the Fermi level of Ag substrate by means of ultraviolet photoelectron spectroscopy \(^25\), and monitored by each of the above-stated compounds, which was deposited on the surface of AgBr layer by putting and drying its aqueous solution on it. It was found that the above-stated compounds decreased the height of the top of the valence band on the surface of AgBr, where some of silver ions at surface kink sites move into interstitial positions to form the positive space charge layer.

In the absence of gelatin, the counter ions were forced to form their salts when their aqueous solutions on the surface of an AgBr layer were dried. In the cases of PMT and BT, their counter ions formed their salts with bromide ions, since the solubility of their silver salts was smaller than that of AgBr. In the cases of TAI and KSCN, an anion of TAI and SCN\(^-\) were forced to form the salts with their counter ions, and could not affect the property of AgBr, since the solubility of silver salt of TAI and AgSCN was larger than that of AgBr.

The above-stated result clearly indicated that photographic stabilizers could work on the surface of AgBr only in the presence of gelatin.

**Ag Cluster Formation by Gelatin**

It is known that gelatin reduces silver ions to form Ag clusters \(^2\). Urabe and Sano emphasized the reducing ability of gelatin by comparing its performance with that of a synthetic polymer without reducing ability \(^8\). In this paper, Ag cluster formation as a result of the reduction of silver ions by gelatin was studied according to the examinations of electrochemical potentials for liquid emulsions and Fermi levels for dried emulsion layers in light of the fact that electrochemical potential of a solution should correspond to Fermi level of a solid.

The formation of silver clusters as the result of the reduction of silver ions by gelatin in liquid emulsions would be represented by the following general reversible reaction.

\[
\text{Red} + n\text{Ag}^+ \leftrightarrow n\text{Ag} + \text{Ox} + m\text{H}^+ \quad (1)
\]

where Red was reduced gelatin, Ox was oxidized gelatin, \(n\) was the number of electrons given up by the reduced gelatin, and \(m\) was the number of protons produced. The equation (1) could be separated into two half-cells, each of which had a characteristic potential associated with it, the silver half-cell, \(E_{Ag}^0\)

\[
\text{Ag}^+ + e^- \leftrightarrow \text{Ag} \quad (2)
\]

and the gelatin half-cell, \(E_{Gel}^0\)
The cell potential for Equation (1) was the difference in potential for the two half-cell reactions,

$$\Delta E = E_{Ag} - E_{Gel}$$  

and the rate of silver cluster formation was approximately expressed as follows, 

$$\frac{dAg}{dt} = [\text{Red}]k^{0}_{Ox}\exp[(1-\alpha)nF\Delta E/RT]$$  

where $[\text{Red}]$ is the concentration of the reduced gelatin, $k^{0}_{Ox}$ is the specific rate of the forward reaction in Equation (1), $\alpha$ is the charge transport coefficient, and $F$ is Faraday. It was predicted from Equations (4) and (5) that Equation (1) should proceed to the right when $\Delta E$ was positive, and its rate should increase with increasing $\Delta E$.

**during Precipitation of AgBr Grains**

The reduction of silver ions by gelatin to form Ag clusters proceeds with positive value of Equation (4), in which $E_{Ag}$ increased with decreasing $pAg$ while $E_{Gel}$ decreased with increasing pH. In order to study the formation of silver clusters during precipitation of AgBr grains, cubic AgBr grains with edge length of about 0.2 μm were precipitated in the presence of deionized gelatin with variation of bulk pH and $pAg$ in a reaction solution. The sensitivities were normalized with respect to the grain sizes, and plotted as a function of pH values of the reaction solutions in Figure 2. It was found that the sensitivity of the grains steeply increased with increasing the bulk pH value in the range from 4 to 10, while it did not depend upon the bulk $pAg$ value. Then, the above-stated emulsion layers were subjected to hydrogen hypersensitization, and the observed sensitivities are plotted as a function of the pH values in Figure 2. As seen in this figure, the sensitivities of all the hydrogen-hypersensitized emulsions were nearly the same with each other, and were nearly equal to the sensitivity of the emulsion prepared at pH10. In the light of the fact that hydrogen hypersensitization is an efficient method to form reduction sensitization centers on silver halide grains in dried emulsion layers, it was judged from the above-stated result that reduction sensitization centers were formed during the precipitation of the grains.

Figure 3 shows the redox potential of an aqueous gelatin solution as a function of pH. The bulk $pAg$ values employed in this study were 50, 100, and 150 mV vs. SCE. It is therefore judged that $\Delta E$ could be positive at pH of around 8 and larger than that. As seen in Figure 2, the increase in sensitivity due to the formation of reduction sensitization centers could be however observed even at pH4. This discrepancy indicated that the formation of reduction sensitization centers did not take place in the bulk of a reaction solution.

On the other hand, the $pAg$ value in the region where an aqueous solution of AgNO$_3$ was introduced in a reaction solution was ~500 mV, and was independent of the bulk $pAg$ values. It is therefore judged that the value of $\Delta E$ in the region where an aqueous solution of AgNO$_3$ was introduced in a reaction solution were positive even at pH4 regardless of the bulk $pAg$ values, and increased with increasing pH. The above-stated result was in good accord with the result shown in Figure 2, and indicated that reduction sensitization centers were formed, not in the bulk, but in the region where an aqueous solution of AgNO$_3$ was introduced in a reaction solution for the precipitation of AgBr grains. The above-stated results revealed that silver clusters were formed during the precipitation of AgBr grains when $\Delta E$ in Equation (4) was positive, and that the rate of the formation increased with increasing $\Delta E$ as indicated by Equation (5).

**during Digestion of AgBr Emulsions**

The formation of silver clusters during digestion of emulsions was initiated by Wood as silver digestion and studied by several groups of workers. In the former paper, an analysis was made on the sensitivities of AgBr emulsions digested at various $pAg$ and pH values. It was observed that the sensitivity was increased when they were digested under the condition with positive $\Delta E$, and that the increase in sensitivity was enhanced by the increase in $\Delta E$. This result also indicated that silver clusters such as reduction sensitization centers were formed during the digestion of AgBr emulsions when $\Delta E$ in Equation (4) was positive.
tive, and that the rate of the formation increased with increasing $\Delta E$ as indicated by Equation (5).

— during Storage of Dried Emulsion Layers

In the former paper 27), fine AgBr grains in emulsions were prepared at pH2 in order to minimize the formation of reduction sensitization centers during their precipitation, and digested at 60°C for 60min in the presence of DMAB (dimethylamine borane) to form reduction sensitization centers on the grains. The sensitivities of these emulsions were plotted as a function of the amount of DMAB in Figure 4. As seen in this figure, the sensitivities increased through two steps with increasing the amount of DMAB. It was concluded that the first step was caused by R centers acting as positive hole traps, and the second step was caused by P centers acting as electron traps.

Then, those emulsion layers were subjected to the study of the formation of reduction sensitization centers during storage of dried emulsion layers. As shown in Figure 4, the sensitivity of the AgBr grains was elevated and became to be nearly equal to that of reduction-sensitized grains when the emulsion layer was kept at 70°C for 3days in Ar atmosphere free from oxygen and water 27). This result indicated that the reduction of silver ions by gelatin (i.e., the electron transfer from gelatin to AgBr grains) to form reduction sensitization centers on the grains took place in dried emulsion layers. This idea was supported by UPS measurement, according to which the Fermi level of a gelatin layer was higher than that of an AgBr layer 5). In the light of the fact that electrons tend to transfer from a phase with higher Fermi level to a phase with lower Fermi level to equalize their Fermi levels when they are in contact with each other, it is considered that silver clusters were formed in dried emulsion layers as a result of the electron transfer from gelatin phase to AgBr grains in emulsions to equalize the Fermi levels between them during the above-stated keeping condition.

Effect of Gelatin on Stability of Emulsions

It is known that reduction sensitization centers increase sensitivity, and cause fogging especially in gold-sensitized emulsions. It is therefore considered that the formation of reduction sensitization centers during storage of emulsion layers deteriorates their keeping stability. Since stabilizers and antifoggants as described before strongly combine with silver ions to form scarcely soluble silver salts and to make $E_{Ag}$ in Equation (4) less positive, they are expected to depress the formation of silver clusters owing to the reduction of silver ions by gelatin and stabilize the photographic behavior of emulsion layers. It was confirmed in the former paper 27) that TAI could stabilize (i.e., depress the changes in sensitivity and fog density of) sulfur-plus-gold-sensitized AgBr emulsions by depressing the formation of reduction sensitization centers during the storage of the emulsions. It should be noted again that TAI could not influence the property of the grains in the absence of gelatin, as shown before.

It has been thus demonstrated that gelatin has essential influences on the stability of emulsions from the viewpoints of adsorption of stabilizers to AgBr grains in dried emulsion layers and Ag cluster formation as a result of the reduction of silver ions by gelatin during storage of emulsion layers.

Requirement for Gelatin from Its Chemical Roles in Emulsions

Although gelatin is indispensable for photographic stabilizers to function, it deteriorates the stability of photographic behavior of emulsion layers by forming reduction sensitization centers as a result of the reduction of silver ions by gelatin during storage of the emulsion layers. From the viewpoint of the design of emulsions, it is desirable that gelatin is inactive with respect to reducing activity and leaves the formation of chemical sensitization centers such as reduction and sulfur sensitization centers to well-controlled chemical sensitization treatments (i.e., digestions of silver halide emulsions in the presence of chemical sensitizers).

References