Physical Restraining Property of Photographic Gelatins (II)

pH Dependence of Physical Retardance of Gelatin Treated with Ion Exchange Resins

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Abstract

The ion exchange treatments changed the pH dependence of physical retardance of photographic gelatins. It was suggested that some ionic substances affecting physical ripening were eliminated by the process. The physical retardance lost in the ion exchange could be partly restored by the addition of adenine and sodium thiosulfate.

§ 1. Introduction

Photographic gelatin plays many roles in the making and processing of a photographic emulsion. The restraining of ripening is the important one of these roles.

The purpose of the present investigation is to make clear the origin of the physical restraining property of photographic gelatins. The authors have already reported that IAG gelatins were assorted into several groups by the pH dependence of restraining ability1). This pH dependence suggests that substances responsible for the restraining are ionic. According to literatures2), highly restraining gelatins contain more nucleic acids and labile sulfur than lowly restraining or unrestraining (inert) ones do. Rousselot3) reported ion exchange treatment made gelatins inert. Itoh4) reported that the physical restraining power due to adenine was eliminated by the ion exchange treatment while that due to nucleic acid was not affected. Ion exchange treatments have also been applied to the separation and determination of thiosulfate in photographic gelatins3,5). The present paper concerns with the use of the ion exchange method on the study of restrainers in photographic gelatins. It was found that both anionic and cationic substances were responsible for the restraining behaviour of gelatins.

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§ 2. The pH Dependence of Physical Retardance of Ion Exchanged Gelatin

2.1 Experimental

1) Ion exchange treatment of gelatin

Cation exchange resin (Amberlite IR 120B) and anion exchange resin (Amberlite IRA 410) were converted into H and OH forms, respectively. Twenty gram sample gelatin was swollen with 100 ml distilled water, dissolved at 70°C, and cooled to make gel. In the case of deionization, 60 g cation exchange resin or 80 g anion exchange resin was added to the gelatin solution, and after 1 hour’s stirring at 40°C, the solution was separated from the resin and cooled to make deionized gel. Highly restraining gelatins (DGF 5294, Stoess 2766, Rousselot 9245, Nelson Dale 2 and Kind & Knox 2006) and lowly restraining one (Rousselot 16448) were used.

2) Preparation of test emulsion

The method is the same as in the previous report1), except scaled down to one-fifth. The emulsion formula is as following.

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\text{Solution A} \begin{cases} 
\text{NaCl (35 g/l)} & 2 \text{ ml} \\
\text{Gelatin gel} & 6 \text{ g} \\
\text{pH adjusting solution} & X \text{ ml} \\
\text{Distilled water} & (5 - X) \text{ ml} 
\end{cases}
\]

\[
\text{Solution B} \begin{cases} 
\text{AgNO}_3 & 17 \text{ g/l} & 4 \text{ ml} 
\end{cases}
\]

Preliminary test confirmed no remarkable change was observed on the pH dependence
Fig. 1. pH dependence of physical retardance of deionized gelatins.
curve of physical retardance with this scale down. In some gelatins, however, the retardance were generally depressed a little by the scale down, but the curve shape was not changed remarkably.

2.2 Results

The results shown in Fig. 1 are summarized as follows. The retardance decreased remarkably in neutral and alkaline pH's and slightly in an acidic pH by the cation exchange treatment (except Nelson Dale 2). The anion exchange treatment decreased the retardance in acidic pH (except Kind & Knox 2006), and in alkaline pH decreased the retardance of Stoess 2776 and DGF 5294 slightly, but increased those of Rousselot 9245 and Nelson Dale 2 a little. Lowly restraining Rousselot 16448 changed little its physical retardance by any ion exchange treatment.

2.3 Discussion

The physical retardance of highly restraining gelatins decreased remarkably by the cation exchange treatment in neutral and alkaline pH's. It seems to show that these gelatins contained such substances as adenine and guanine which act restraining in neutral and alkaline pH's, and that the cation exchange has eliminated these substances4,7. The reason why the retardance did not decrease so much in acidic as in alkaline pH may be ascribed to the presence of nucleic acids which are restraining but not eliminated by the cation exchange treatment. Since thiosulfate is not eliminated by the cation exchange treatment, it may act as physical ripening accelerator in alkaline pH5.

In the case of the anion exchange treatment, the retardance decreased slightly in acidic and alkaline pH's (except Kind & Knox 2006). The anion exchange treatment must have eliminated thiosulfate in the photographic gelatins as in the case of quantitative determination of thiosulfate in gelatin5,4. Also some other impurities are probably eliminated. In acidic pH thiosulfate may act as a restrainer, and in alkaline pH as an accelerator of silver-chloride growth.

The pH dependence of physical retardance of Kind & Knox 2006 is different from the other ones. The reason is not clear. Rousselot 16448 did not change its restraining property by the ion exchange treatment. It is likely that this gelatin contains little restraining and accelerating substances to be eliminated by the treatments; this gelatin showed low restraining all over the pH range.

It is concluded that the ion exchange treatment has changed the ratio of restraining substances to accelerating substances in gelatin, hence the change in the pH dependence of physical retardance of deionized gelatin.

§ 3. Recovery of the Lost Physical Retardance of the Deionized Gelatin by the Addition of Adenine and Thiosulfate

3.1 Experimental Method

Stoess 2766 gelatin, which is highly restraining over a wide pH range and whose retardance is changed remarkably by the ion exchange treatment, was chosen as an appropriate sample. Adenine and/or thiosulfate dissolved in distilled water were added to the solution A in the physical retardance determination. Addition of distilled water was adjusted so as to keep the gelatin concentration constant.

3.2 Results and Discussion

1) Addition of adenine to cation exchanged gelatin

By the addition of adenine to the cation exchanged gelatin, the physical retardance increased in neutral and alkaline pH's, and the degree of the enhancement increased with the increase in added adenine as shown in Fig. 2. Although adenine was effective to increase the retardance in neutral and alkaline pH's addition of adenine by itself was not sufficient to recover the gelatin's original retardance all over the pH ranges tested, therefore we looked for other restraining substances that might have been eliminated by the cation exchange treatment. It seems that high molecular-weight substances such as nucleic acids were not eliminated by the cation exchange treatment.

2) Addition of thiosulfate to the anion exchanged gelatin

By the addition of the thiosulfate to the
anion exchanged gelatin, the physical retardance decreased in alkaline pH, but increased slightly in acidic pH as shown in Fig. 3. When thiosulfate was added in quantities enough to recover the retardance in acidic pH, the retardance fell to a lower level than that of the original in alkaline pH. It seems that not only thiosulfate but also other substances were responsible for the retardance in alkaline pH and they have been eliminated also by the anion exchange treatment.

3) Addition of both thiosulfate and adenine to the cation and anion exchanged gelatin

The addition of adenine and thiosulfate made the retardance recovered over a wide pH range except at about pH 6, and an increased addition of adenine recovered the retardance at that point too, as shown in Fig. 4. But in all the cases the retardance

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Fig. 2. pH dependence of physical retardance of cation exchanged Stoess 2766 on adenine addition.

--- original gelatin
---- cation exchanged gelatin
Numbers on curves indicate addition of adenine to the cation exchanged gelatin.
(1) 1 mg/g (2) 0.4 mg/g (3) 0.1 mg/g
(4) 0.05 mg/g

Fig. 3. pH dependence of physical retardance of anion exchanged Stoess 2766 on sodium thiosulfate addition.

--- original gelatin
----- anion exchanged gelatin
Numbers on curves indicate addition of sodium thiosulfate to the anion exchanged gelatin.
(1) 0.012 mg/g (2) 0.024 mg/g (3) 0.048 mg/g

Fig. 4. pH dependence of physical retardance of both cation and anion exchanged Stoess 2766 on adenine and sodium thiosulfate addition to the deionized gelatin

--- original gelatin
------ cation and anion exchanged gelatin
Numbers on curves indicate addition of adenine and sodium thiosulfate to the deionized gelatin.

adenine sodium thiosulfate
(1) 0.4 mg/g 0.024 mg/g
(2) 0.4 mg/g 0.048 mg/g
(3) 0.2 mg/g 0.024 mg/g
(4) 0.2 mg/g 0.048 mg/g
(5) 0.05 mg/g 0.024 mg/g
(6) 0.05 mg/g 0.048 mg/g
could not be recovered in full detail. Therefore, it is likely that other substances have also been eliminated by the ion exchange treatments.

§ 4. Summary

Highly restraining gelatins changed remarkably their pH dependence of physical retardance by the ion exchange treatment; the physical retardance decreased notably in neutral and alkaline pH's, and slightly in acidic pH by the cation exchange treatment. This shows that the substances which restrain the physical ripening in alkaline pH are eliminated but those restrain in acidic pH are not eliminated by the treatment. By the anion exchange treatment of highly restraining gelatin, the physical retardance decreased slightly in acidic and alkaline pH's. The anion exchange probably eliminated thiosulfate and other substances.

It is concluded from the above results that the highly restraining gelatins contained ionic substances which were eliminated by the ion exchange treatment and thus the balance of ripening accelerator and restrainer in gelatin was changed. As a result, pH dependence of physical retardance was changed.

In the case of lowly restraining gelatin the physical retardance was not changed significantly by the ion exchange treatment. It suggests that the gelatin contains little ionic restraining and accelerating substances.

Adenine was effective to increase the physical retardance in neutral and alkaline pH's but not in acidic pH. Thiosulphate made the physical retardance rise slightly in acidic pH, but accelerated physical ripening in neutral and alkaline pH's. Addition of both thiosulfate and adenine to the deionized gelatin additively increased the physical retardance. It recovers the physical retardance of ion exchanged gelatin approximately to the original type.

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