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Abstract

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ON THE PHOTOGRAPHIC ACTIVITY OF GELATIN

It is known that the source of the photographic activity of gelatin is certain impurity substances possessing a chemical affinity for silver ions and interacting with the solid phase of the emulsion. This is revealed especially convincingly, on the one hand, in the study of the binding of Ag^+ ions by gelatin and, on the other, in experiments on the action of certain ion-exchange resins on a gelatin solution.

A study of the kinetics of the interaction of silver nitrate with gelatin in solution led to the conclusion ([1]) that the active impurities include three types of substances: substances forming thermally stable silver complexes, compounds with labile sulfur, and reducing agents. Study of the dependence of bound Ag^+ ions on their concentration in solution shows ([2,3]) that gelatin contains two groups of complex-forming substances: one consists of compounds with the greatest affinity for Ag^+ ions, with which they form thermally stable and irreversible complexes; the other includes compounds with lower affinity, also forming thermally stable but reversible complexes (having a solubility product greater than that of AgJ). The nucleation substances present in gelatin (compounds with labile sulfur and reducing agents) possess still less affinity for Ag^+ ions; it is therefore natural to expect that the rate of chemical ripening is linearly related to the magnitude of the ratio of the amounts of complex-forming substances of the first and second types (the activity coefficient) and is not in simple dependence on the content of sulfur compounds and reducing agents, as is evident from Table 1.

Table 1

Fig. 1

Figure 1: Fig. 1

Nos. of gelatin samples GKhZ	Compounds with labile sulfur	Reducing agents	Complex-forming compounds, accelerating ripening (a)	Complex-forming compounds, destroying ripening centers (b)	Activity coefficient $k\frac{a}{b}$	Time to reach $S_{\max}$, τ_0 (min.)	Final value $H - k\tau_0$	Calculated value τ_0 (mean $H = 88$)
463	60	3	13	20	0,65	150	98	135
6768	76	5	10	20	0,50	180	90	175
6769	61	23	10	20	0,50	180	90	175
1101	33	22	16	35	0,46	180	83	190
7166	80	33	4	10	0,40	210	84	220
7188	32	34	8	25	0,32	270	86	275
479	42	29	5	18	0,28	300	84	315

For studying the role of impurity substances in the process of chemical ripening, experiments were carried out to remove them from gelatin by means of adsorbents and to isolate them by electrodialysis. Various adsorbents posses–

have a selective action, and only some ion-exchange resins (“vofatit M^+,” AN-1) proved capable of removing practically all the active impurities. As a result, the various gelatin samples acquired identical properties, turning into gelatin that acts slowly at the stage of chemical ripening (inert) (see Fig. 1). Analysis showed that after such purification only an insignificant amount of reducing agents was detected in the gelatin ($\sim 4.0 \cdot 10^{-7}$ g-equiv. per 1 g of gelatin).

Fig. 1. Kinetics of chemical ripening of photographic emulsions. **A** –before purification, **B** –after purification. **1** –sample No. 418, **2** –No. 7174, **3** –No. 3516, **4** –No. 456, **5** –No. 1856.

Electrodialysis also removes active impurities and converts gelatin into an inert form (see Fig. 2). When a five-chamber apparatus is used, electrodialysis makes it possible to separate impurity substances in the form of cathode and anode fractions. Study of these solutions made it possible to establish that the substances of the cathode fraction do not enter into irreversible interaction with silver ions, whereas compounds with labile sulfur, reducing agents, and complex-

Fig. 2

Figure 2: Fig. 2

forming substances of the first type pass into the anode fraction. The analytical data on the impurity substances of the anode fraction are given in Table 2.

Fig. 2. Kinetics of chemical ripening of photographic emulsions. **A** —before electrodialysis, **B** —after electrodialysis. **1** —sample No. 12240, **2** —No. 418, **3** —No. 443, **4** —No. 482.

A photographic test showed that the solution of the cathode fraction has a ripening-retarding function, whereas the solution of the anode fraction has an accelerating function. Figure 3 presents kinetic curves of the change—

Table 2

Amount of impurity substances (in g-eq. $\times 10^7$ per 1 g of gelatin)

Gelatin sample Nos.	In gelatin before electrodialysis: total	In gelatin before electrodialysis: compounds with labile sulfur	In gelatin before electrodialysis: reducing agents	In gelatin before electrodialysis: complex-forming compounds	In anodic fraction: total	In anodic fraction: compounds with labile sulfur	In anodic fraction: reducing agents	In anodic fraction: complex-forming compounds
KZhZ$' 482|39|20|19|0|17|6|11|—||*KZhZ*' $443	70	56	6	8	24	13	11	—
Amer. 12 240	90	50	25	15	45	17	17	11

changes in photosensitivity and the growth of fog upon introducing into one gelatin, at the stage of chemical ripening, one or the other of the fractions isolated from

Fig. 3. Influence on the kinetics of chemical ripening of photographic emulsions of impurities of the anodic and cathodic fractions isolated from fast (**A**) and slow (**B**) gelatin. **1** —control emulsion, **2** —emulsion with an impurity of the anodic fraction, **3** —emulsion with an impurity of the cathodic fraction.

fast and slow gelatin. From the displacement of the curves it is evident that in the first gelatin accelerators predominate, whereas in the second—ripening inhibitors. These results are in agreement with the conclusion that the rate of chemical ripening depends on the ratio of complex-forming substances of the first and second types, which possess the greatest affinity for Ag^+ ions.

Thus, a general conclusion may be drawn that the photographic action of gelatin during ripening is effected by two of its components: macrocomponents—the protein substance of gelatin, possessing protective properties and a certain reducing function—and microcomponents, whose role is reduced mainly to regulating the rate of chemical ripening.

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CITED LITERATURE

1. A. A. Titov, I. M. Ratner, *Tr. Nauchno-issl. kino-foto inst.*, **8**, 20 (1948).

2. A. A. Titov, ibid., **8**, 41 (1948).

3. A. L. Karpov, Yu. Sh. Moshkovskii, *ZhFKh*, **28**, 1746 (1954).

Note: Figure translations are in progress. See original paper for figures.