Grain Growth of Silver Chloride Suspensions in Polyvinyl Alcohol

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Introduction

Aqueous suspensions of silver chloride in the presence of protective colloid such as gelatin are usually called emulsion in photography. It is well known that grains of silver halide formed by mixing silver nitrate solution with alkali halide solution quickly coagulate and precipitate when the protective colloid is absent. In the aqueous solution of gelatin, not only is this coagulation or precipitation inhibited, but the grain growth is also retarded. The grain-growth, however, is not so completely inhibited as in polyvinyl alcohol described later, but is smooth enough to fulfil the requirements of emulsion-making in the photographic industry.

On the contrary silver halide emulsions prepared with polyvinyl alcohol as protective colloid consist of very fine grains not exceeding 0.1 μ and 0.05 μ in diameter for bromide and chloride respectively. They scarcely grow by the prolonged ripening at rather high temperature, because the grain-growth is inhibited by its extraordinarily strong adsorption to the silver halide grain and the lack of active substances ordinarily found in gelatin. The function of these active substances is to accelerate the grain-growth. In the following, the role of these substances is disscussed.

The author reported previously⁽¹⁾ that it becomes very turbid as soon as traces of some sulfur-containing substances are added to the suspension, and this increase in turbidity is the evidence of grain growth in the suspension. This was confirmed by the electron micrograph. The amount of addition necessary to produce the increase of turbidity (i.e. the growth of grains) differs very widely from one to another. This grain-growth can easily be traced by the nephelometric method, and can be described as functions of time and temperature of ripening and amounts of active substances added. Substances tested and reported in the previous paper are limited only in some sorts of sulfur-containing compounds known as chemical sensitizers in photography, e.g. thiosinamine, thiosulphates, rhodanine, the N-alkyl-thiones of Kendall⁽²⁾ and their derivatives. These substances, however, with few exceptions, produce heavy fog during ripening from lack of stability of the complex compounds with silver halide.

In this paper the author will present some other types of active substances, much more important for the investigation of physical

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1) Y. Ohyama, Royal Photographic Society Centenary Conference, London, Sept. (1953) (Proceeding is now in press).

2) J. D. Kendall, 9th Internat. Congress of Phot., Paris, 235 (1935).

ripening of photographic emulsion and for the understanding of the role of gelatine. They do not produce fog but increase stability of the emulsion in many cases. Compounds now investigated include a large number of substances not containing active sulfur, e.g. N-alkyl homologues of guanidine, pyrrolidone, pyridone, quinolone, 2-iminobenzothiazoline, etc. High molecular compounds such as polyvinyl pyrrolidone or albumin have also been tested and their activities are confirmed.

Experimental

The grain-growth can be traced by the nephelometric method as was previously reported[1], because in the region of the sizes in question (between 0.05 μ and 0.25 μ in diameter) it was confirmed by Evva[3] and Ammann-Brass[4] that the increase of turbidity of the suspension is in linear proportion to the mean graindiameter. To 42 ml. of aqueous solutions of active substances with varying concentration (10 ml. of this solution may be replaced by alcohol if needed for substances sparingly soluble in water), 10 ml. of 6% solution of polyvinyl alcohol and 4 ml. of 0.6 M NaCl solution are added. The mixture is heated to 70°C, and 4 ml. of 0.2 M silver nitrate solution (70°C) is added in 15 seconds. After drawing out 2 ml. of this suspension of AgCl at 2, 4, 8 and 16 min. after the addition of silver ions, it is diluted with 20 ml. of cold water and the turbidity is measured. This is done by measuring the intensity of a parallel light beam which passes through a glass cuvette (1 cm. depth) containing the diluted suspension with the aid of a photocell at two points: just behind the cuvette and 20 cm away from it. Afterwards this rather complicated method was replaced by a simple measurement of optical absporption and this is designated as the transmission method.

In the previous report[1], dealing with sulfur-containing chemical sensitizers, the addition of active substances was effected after the emulsification (formation of fine suspension of silver chloride) was accomplished. In this report, however, the addition was effected before the emulsification except for the case specially cited. Usually this has no influence upon the turbidity obtained at the same period of ripening and also the activity of the substance used is identical. The new method is very convenient for the experiments at high concentration and particularly suitable for a thermally coagulating substance such as albumin.

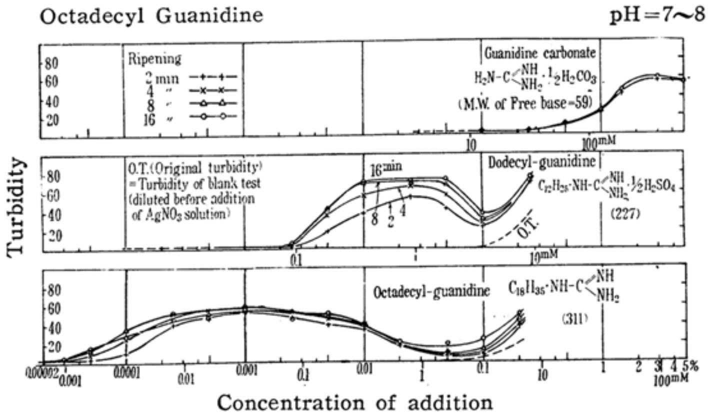

Fig. 1. Ripening characteristics of guanidine derivatives (Part. 1).

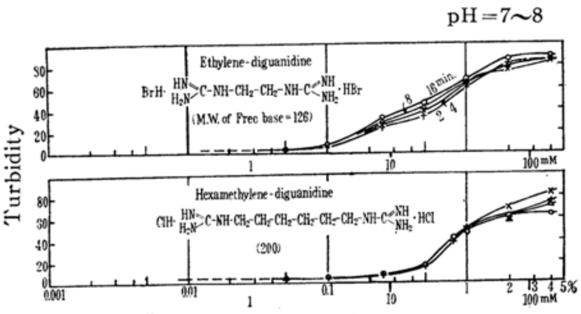

Fig. 2. Ripening characteristics of guanidine derivatives (Part. 2).

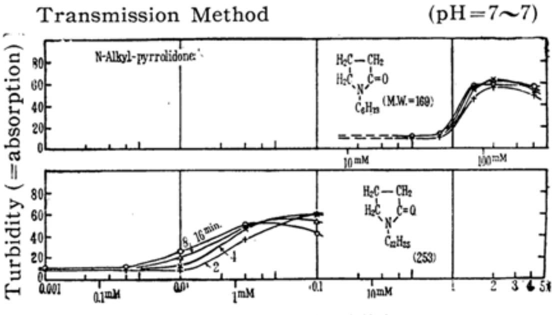

Fig. 3. Ripening characteristics of pyrrolidones.

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[3] F. Evva, *Z. wiss. Phot.* **47**, 39, (1952).

[4] H. Ammann-Brass, *Sci. et Ind. Phot.*, [2], **23**, 249, (1952).

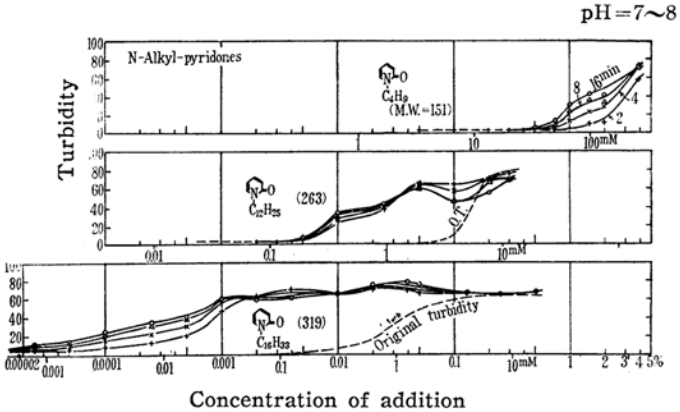


Fig. 4. Ripening characteristics of pyridones.

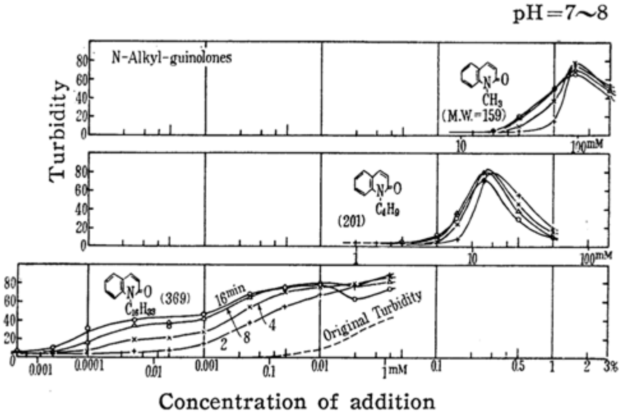


Fig. 5. Ripening characteristics of quinolones.

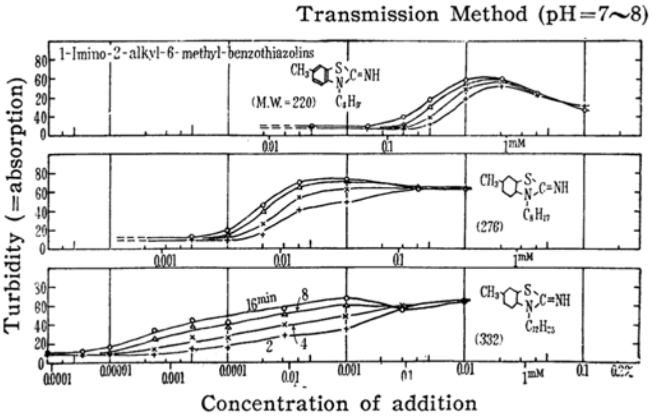


Fig. 6. Ripening characteristics of 2-imino-thiazolines.

Results and Discussion

(a) Ripening Characteristics.—If turbidity is plotted against the concentration (on logarithmic scale) of added substance in the emulsion, taking ripening (or heating) time as parameter, characteristic curves of many substances are obtained. Using these diagrams, comparisons of their activities and also ripening characteristics at various concentrations are easily recognizable at a glance. Fig. 1, and Fig. 2 show some examples of these characteristic curves of the guanidine series. Fig. 3, 4, 5 and 6 are those of pyrrolidone, pyridone, quinolone and 2-imino-thiazoline series respectively.

(b) Activity and its Dependance on Molecular Weight.—Activity defined as the reciprocal of the minimum addition concentration (in milli mol.) which causes definite turbidity-increase is valuable for the comparison of the activities of many substances and can also be used for the determination of the relation between activity and the molecular weight or the chemical constitution of active substances. The choice of the comparison point may be optional, turbidity increase of 2, 10, 20 or 40 units (or absorption of 15, 20, 30 or 40% for transmission method) are convenient and usually 10 unit increase (or absorption of 20%) was preferred.

Fig. 7, 8 and 9 show the relation between activities and molecular weights of N-alkyl homologues of the above mentioned substances. Symbols of G, PQ and IT represent guanidine, pyridone (and also pyrrolidone) quinolone and 2-imino-thiazoline series respectively. It is very astonishing to know that activities in these several series of substances increase markedly with increasing molecular weight by introducing alkyl radicals of increasing numbers of carbon atoms. The relation between activity (A) and molecular weight (M) can be expressed approximately in the following equation,

$$\log_{10}A = \frac{M}{50} - \alpha$$

where α is constant in each series. The equation states that the increase in molecular weight by 50 enhances the activity 10 times in each series of substances. It is varied as far as the molecular weight reaches 300–400.

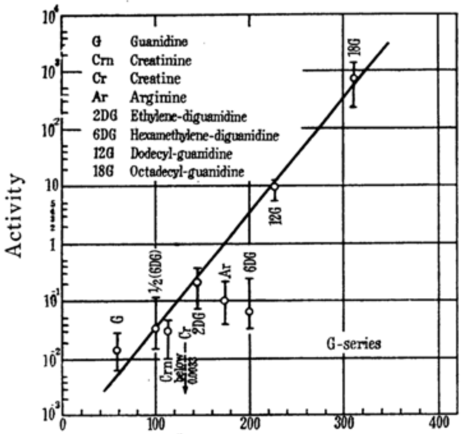


Fig. 7. Relation between activities and molecular weight of guanidine series.

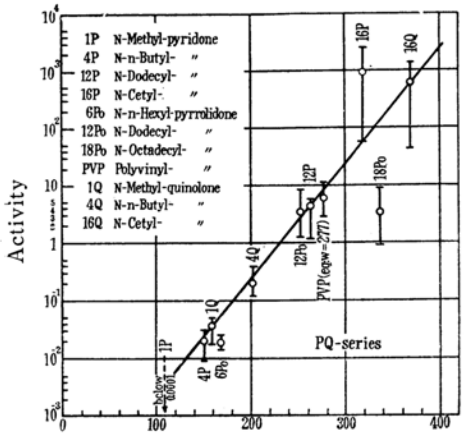


Fig. 8. Relation between activities and molecular weight of pyrrolidone, pyridone and quinolone series.

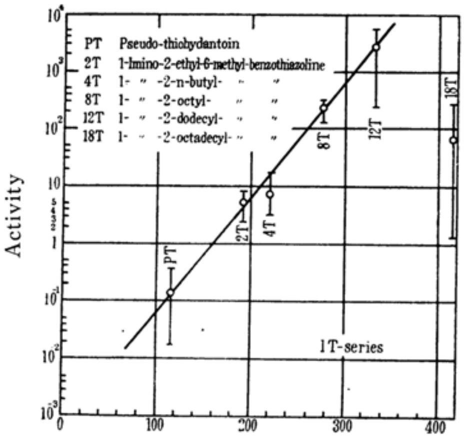
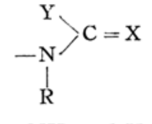


Fig. 9. Relation between activities and molecular weight of imino-thiazoline series.

(c) General Constitution of Active Substances.—The above mentioned active substances have the following general chemical constitution,



where X is O or NH and Y is $-NH_2$, $-NH-$, $-N=$, $-CH=CH-$, $-CH_2-CH_2-$, $-O-$, $-S-$, or radicals constituting heterocyclic ring with N atom adjacent to central carbon atom. R is alkyl, aryl or aralkyl radical usually up to 20 carbon atoms. It is interesting to recall here that sulfur containing active substances previously reported by the author[1], with few exceptions have chemical constitution in accord with this general structure if X is taken as S, for example thioacetanilide, isothiocyanates, thiourea derivatives, rhodanines or the N-alkyl thiones of Kendall[2].

Of course, there are many active substances which do not coincide with the above mentioned general constitution such as thiosulphates, xanthates, alkylamines, heterocyclic amines or many thiol compounds. Some of them were reported already[1] and others will be reported in another paper.

(d) **Polyfunctional Derivatives and Effective Molecular Weight.**—As is shown in Fig. 7, the activity and molecular weight relation for hexamethylene-diguanidine is irregular whereas ethylene-diguanidine is regular, and if the molecular weight of hexamethylene-diguanidine is divided by 2, the position of the substance falls just on the line and we are able to conclude that the effective equivalent weight of hexamethylene-diguanidine is one half of its real molecular weight.

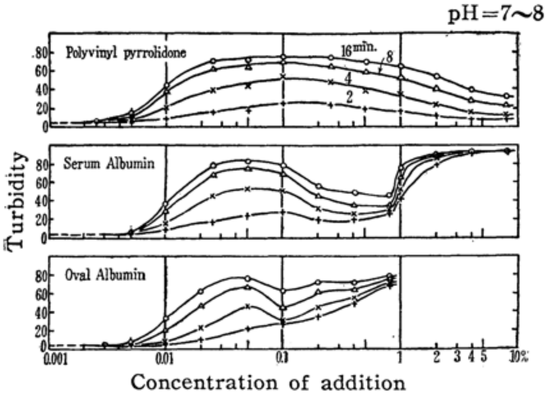


Fig. 10. Ripening characteristics of albumins and polyvinyl-pyrrolidone.

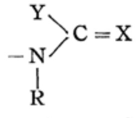
It supports the assumption that hexamethylene-diguanidine adsorbs, on the surface of silver chloride particles, by both active functional ends, whereas ethylene-diguanidine cannot bend enough, because of the shorter chain length. Polyvinyl-pyrrolidone is also active and is almost 10 times as powerful as ordinary active gelatine, and the grain-growth of silver chloride suspension in the mixture with polyvinyl-alcohol is very smooth and rapid as in a gelatinous solution (usual photographic emulsion). The ripening characteristic curve is shown in Fig. 10 and it is possible to estimate the effective equivalent weight of polyvinyl-pyrrolidone from the relation between activity and molecular weight of pyrrolidone derivatives (Fig. 8). The figure obtained is about 277* and it means that every one, two or three pyrrolidone radicals in this long chain molecule** adsorb to the surface of silver chloride. It is interesting to notice that ripening characteristic curves of oval and serumalbumin (also shown in Fig. 10) closely resemble that of polyvinyl-pyrrolidone, considering that their chemical constitutions differ so far and the latter may also be used as an artificial substitute for the former in medical application.

(e) **Influence of Carboxyl Group and Amide Linkage.**—Also in Fig. 7 data on some amino acids having guanyl group, such as arginine, creatine and creatinine are shown. Arginine is not so active as is expected from its molecular weight, and creatine is practically inactive (if active, its activity is below 0.003), whereas creatinine is fairly active (a little below the line). This means that the carboxyl group hinder the activity to a great extent and the amide linkage has scarcely any influence on the activity.

Conclusions

(1) Many substances which accelerate the grain growth of silver chloride suspension in polyvinyl-alcohol were found. Most of them are organic compounds having in their molecule at least one sulfur atom or one nitrogen atom. The most simple compounds are mercaptans or amines of the aliphatic or aromatic series.

(2) Many of them are, however, more complicated compounds having general chemical constitutions as follows,



where X is O, NH, or S, and Y is NH_2; $-NH-$, $-N=$, $-CH=CH-$, $-CH_2-CH_2-$, $-O-$, $-S-$ or radicals constituting the heterocyclic ring with N atom adjacent to central C atom. R is alkyl, aryl or aralkyl radical usually up to 20 C atoms (or vinyl radical for polyvinyl compounds).

(3) Their activities, difined as the reciprocal of the minimum added concentration (in milli mol.) which causes definite turbidity increase, differ very widely from one to another, and increase with increasing numbers of C atoms in R of above general constitutions up to about 16–20 atoms.

(4) The relation between activity (A) and molecular-weight (M) can be expressed in the equation.

$$\log_{10}A=\frac{M}{50}-\alpha$$

(5) Activities of polyfunctional compounds fit more reasonably to the above equation

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* The sum of atomic weight of one unit vinylpyrrolidone is 111 and $277=\frac{1}{2}(2\times111+3\times111)$

** The sample used in this experiment is Albigen, which have a molecular weight of about 25,000.

in which molecular weight is replaced by the effective equivalent weight, which is defined as the molecular weight divided by the number of effective functional groups. And from this effective equivalent weight the mode of adsorption of the active substance can be estimated.

(6) Usually at about a molecular weight of 300–400, the activity for acceleration of the grain-growth reaches its maximum, where the grain-growth of AgCl suspension in polyvinyl-alcohol will take place at very low concentration (about 0.0003 mM≒0.00001%) of an active substance.

(7) From these and other evidences, it may be concluded that in most cases acceleration of the grain-growth is optimum when only the surface of grain is partially covered (at least a few %) with active substances, and the remainder of the surface is occupied by the adsorbed layer of polyvinyl-alcohol.

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