Reasons for Reciprocity Failure at Very Short Exposure Times

By HENRI SAUVENIER

A fine-grain AgBr emulsion, prepared with an inert gelatin, shows no reciprocity failure at very short exposures if the chemical aging has been effected in the absence of $S^=$-unstable ions. In an emulsion with coarse grains (which has therefore undergone the physical aging) there is considerable reciprocity failure. This is due to the fact that the surface-to-volume ratio in these emulsions is smaller than in those with fine grain, so that a gelatin which is inert for the latter is not so for an emulsion with coarse grains. If AgI is added to a fine-grain AgBr emulsion which showed no reciprocity failure, there appears a considerable reciprocity failure at very short exposures.

LET US recapitulate, first of all, what reciprocity failure actually is, with strong illumination (and, consequently, with very short exposure time).

Let us assume that a given density D is obtained through the use of a certain luminous energy E for an exposure time t_1 and an illumination I_1, so that $E = I_1t_1$. If we work with an illumination $I_2 > I_1$ and correspondingly we reduce t ($t_2 < t_1$), so as to make the product I_2t_2 equal E at all times, we get a density less than D. In other words, in order to obtain the same density D with an exposure time $t_2 < t_1$, we have to use an illumination $I'_2 > I_2$. The illumination I and the exposure time t thus do not vary in inverse ratio to each other; we call this a reciprocity failure.

To study this reciprocity failure, we plot Hurter and Driffield curves, $D = f$ (log I), for a certain number of values of t. There is one curve for each value of t. We select a reference density (e.g., 0.1 above fog level) and we mark on each curve the values of I and t which give the reference density. Then we plot a graph with log It as ordinates and log t as abscissas. If there is no reciprocity failure, the representative line is a straight line that runs parallel with the axis of the abscissas (cf. Fig. 1 where the lines are substantially parallel to the log t axis). If there is a reciprocity failure on the strong illumination side, we will get a curve with a negative slope (cf. Fig. 4).

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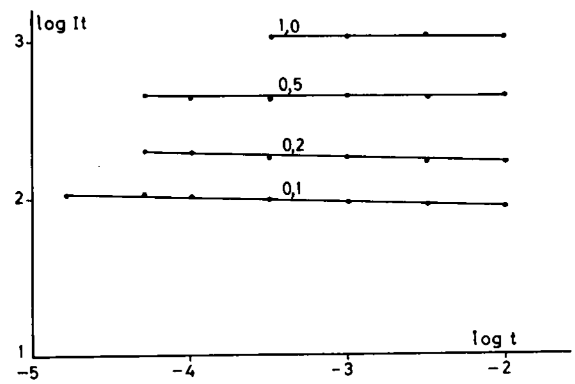

Fig. 1. Reciprocity failure curves for various values of density above fog level. Primary AgBr emulsion, fine grain.

In consideration of the above facts, we plotted the curves of reciprocity between 10^{-2} and 10^{-5} sec of a series of emulsions that satisfies the following conditions.

A. AgBr emulsions prepared with an inert gelatin and not aged physically, and with a grain size about 0.2 micron. These emulsions have not undergone any aging in remelting; they are referred to as primary emulsions. Others have been aged in remelting, without any addition or after the addition of a sulfurizing or reducing sensitizer or of a gold salt.

B. Similar emulsions, but aged physically, with a grain size of approximately 0.8 micron.

C. Fine-grain emulsions prepared with an active gelatin.

D. AgBr suspensions obtained from an aqueous sol of AgBr; grain size, 0.2 micron. Some of these suspensions were obtained by adding the inert gelatin at 35 C and immediate gelling; others underwent the chemical sensitization in the sol first, and then the gelatin was added.

E. AgBr + AgI (0.5 to 5%) emulsions, prepared as indicated in *A*.

The reciprocity curves give the values of log It as a function of log t for four values of the density above fog level (0.1, 0.2, 0.5 and 1). The development was of the surface type (glycin without sulfite for 5 min at 18 C).

Emulsion A: Figure 1 shows that for the primary fine-grain AgBr emulsion no measurable reciprocity failure makes its appearance out to 10^{-5} sec (these emulsions do not possess sufficient sensitivity to allow shorter exposure times to be used with the light levels available).

If the same emulsion is simply aged in remelting, the sensitivity and the reciprocity curve do not differ to any notable extent (the pertinent graph is not reproduced here).

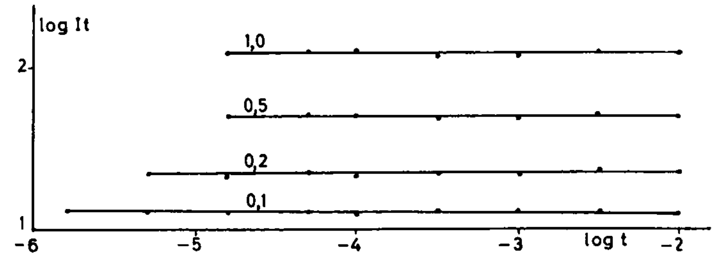

Fig. 2. Primary AgBr emulsion, fine grain, gold sensitized.

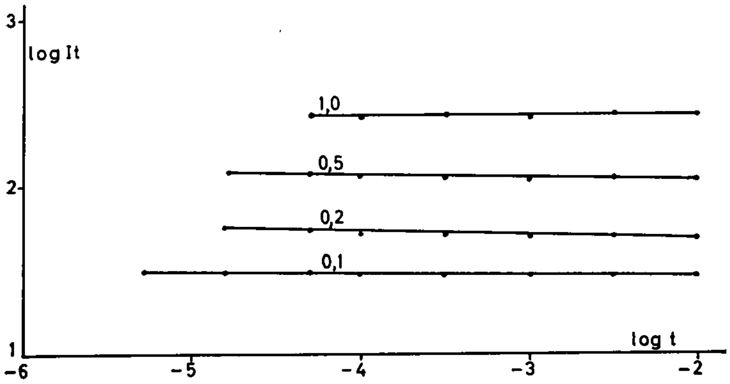

Fig. 3. Primary AgBr emulsion, fine grain, sensitized by reduction.

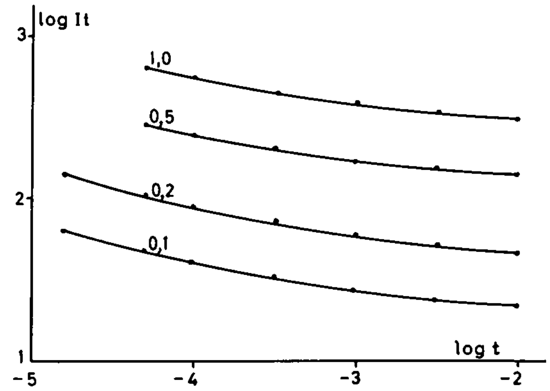

Fig. 4. Primary AgBr emulsion, fine grain, sulfur sensitized.

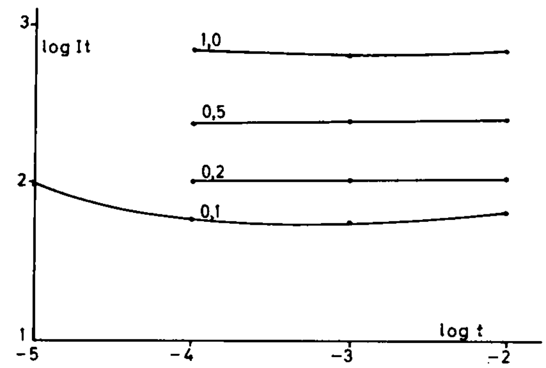

Fig. 5. Physically aged AgBr emulsion, not aged by remelting, coarse grain.

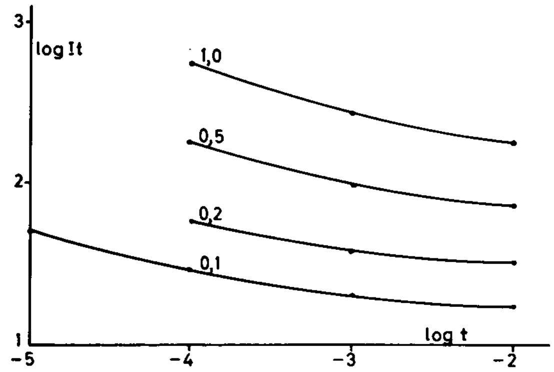

Fig. 6. Physically aged AgBr emulsion, aged by remelting, coarse grain.

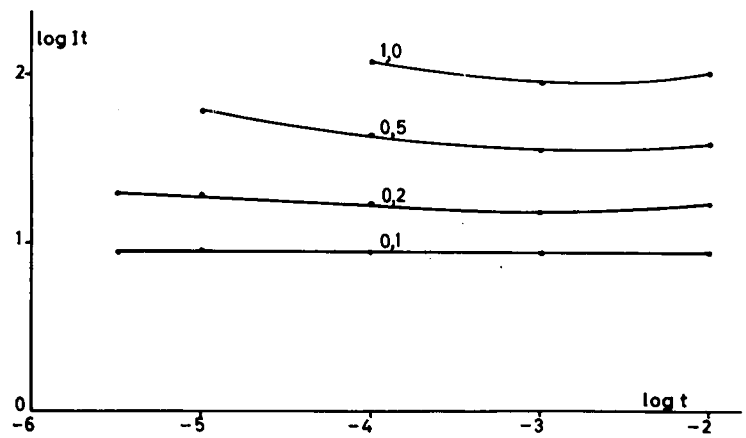

Fig. 7. Physically aged AgBr emulsion, aged by remelting after addition of gold chloride, coarse grain.

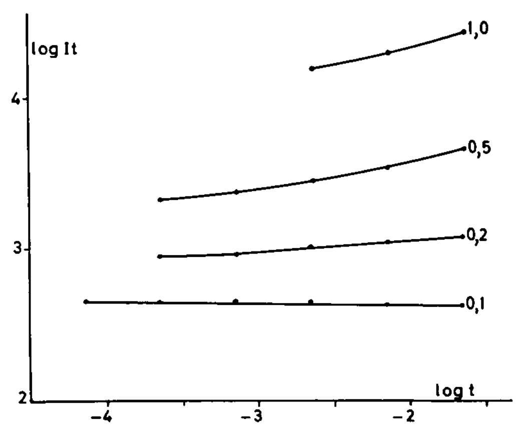

Fig. 8. Primary AgBr suspension, nonsensitized, gelatin added later.

If the same emulsion is sensitized by $AuCl_3HCl$ or by reduction, its sensitivity is increased (see Figs. 2 and 3, respectively) by a factor of the order of 3 to 10, but no noticeable reciprocity failure appears out to 10^{-6} sec.

If the same emulsion is sensitized by $KAu(SCN)_2$, the reciprocity failure is slight. (The pertinent graph is not reproduced.)

If the same emulsion is sensitized by sulfurization (sodium thiosulfate) a reciprocity failure appears between 10^{-2} and 10^{-5} sec (Fig. 4); at the low densities (0.1 to 0.2) the sensitivity is reduced by a factor of the order of 4 as we pass from 10^{-2} to 10^{-5} sec; the loss of sensitivity is a little less for the densities from 0.5 to 1.

We may therefore conclude that with a primary, physically not aged, AgBr emulsion, whether or not aged in the remelting, no significant reciprocity failure makes its appearance for exposure times as short as 10^{-5} sec; the same statement holds true if the emulsion has been sensitized by reduction or by gold salts. The sulfurizing sensitization is accompanied, however, by a reciprocity failure below 10^{-2} sec. These results have been verified on several sets of emulsions.

Emulsion B: The behavior of physically aged AgBr emulsions seems to be different. If the emulsion is not aged in remelting (Fig. 5), the reciprocity failure, negligible out to 10^{-4} sec, manifests itself at shorter times of exposure. An aging in remelting of 3 hr 45 min at 48 C increases the sensitivity and creates quite a considerable reciprocity failure below 10^{-2} sec (Fig. 6). If the aging in remelting is done after the addition of gold chloride, the sensitivity is increased still more, but the reciprocity failure is reduced considerably (Fig. 7).

The gelatin of the emulsions A and B is the same; while it acts as inert with fine-grain A emulsions, it is no longer inert with the coarse-grain B emulsions, because the simple aging in remelting does not affect the sensitivity of A, but it increases that of B. The reason is that a trace of the sulfurizing sensitizer is still sufficient to sensitize somewhat a B emulsion that is coarse-grained and therefore has little specific surface, while it has no effect on an A emulsion the specific surface of which is many times larger. This sulfurizing sensitization already has a certain effect during the physical aging, but it is effective above all when the emulsion is aged in remelting. Since the sulfurizing sensitization introduces a reciprocity failure at the strong illuminations, it is normal for the B emulsion aged in remelting to have an increased reciprocity failure in comparison with an identical but not aged emulsion. This reciprocity failure is reduced by gold sensitization ($AuHCl_4$).

Emulsion C: These conclusions are confirmed by the behavior of fine-grain (or coarse-grain) AgBr emulsions prepared with the aid of a photographic gelatin containing sulfurizing sensitizers; a reciprocity failure always occurs below $t = 10^{-2}$ sec. The magnitude of this failure seems to depend on the quantity of the sulfurizing agent, but is modified by the presence of other chemical sensitizers.

Emulsion D: The case of the AgBr suspensions is particularly interesting, because the sensitizing agents have acted on the AgBr in the absence of gelatin in the aqueous solution only. The curves of reciprocity could not be plotted below 10^{-5} sec because the sensitivity of these suspensions did not permit it with the apparatus available.

For the nonsensitized and therefore primary suspension, Fig. 8 shows a reciprocity failure of the faint illumination type (positive slope). The optimum sensitivity is found in the vicinity of 10^{-4} or 10^{-5} sec, at least for reference densities in excess of 0.1.

If the suspension is aged in remelting after the addition of inert gelatin, it is shown by Fig. 9 that this reciprocity failure becomes much smaller, or even ceases to exist (for small densities); although the aging in the inert gelatin produces only a slight modification of the sensitivity of the suspension for $t = 10^{-2}$ sec, it increases the sensitivity perceptibly for $t = 10^{-5}$ sec (compare the values of the ordinates).

The sensitization by $AuCl_3$ or $KAu(SCN)_2$ increases the sensitivity and produces a very slight reciprocity failure between 10^{-2} and 10^{-5} sec (the pertinent graphs are not reproduced here). The same statement holds true for the sensitization by reduction (Fig. 10).

On the other hand, sulfurizing sensitization (thiosulfate) causes the appearance of a reciprocity failure on the side of *strong* illuminations, below 10^{-2} sec (Fig. 11).

We witness here a crucial demonstration of the action of the sulfurizing sensitizer as a generator of reciprocity failure on the side of strong illuminations, since it transforms the reciprocity failure in the direction of faint

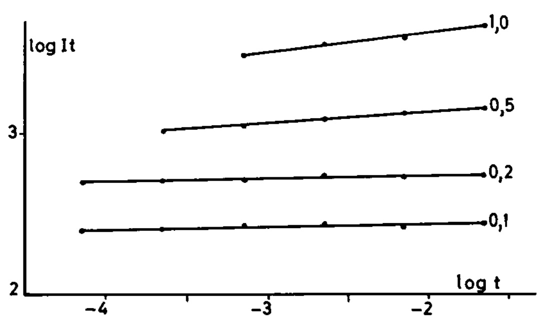

Fig. 9. AgBr suspension similar to that of Fig. 8, but aged by remelting after the addition of inert gelatin.

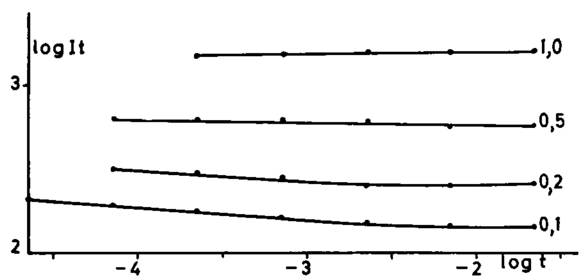

Fig. 10. AgBr suspension similar to that of Fig. 9, but sensitized by reduction.

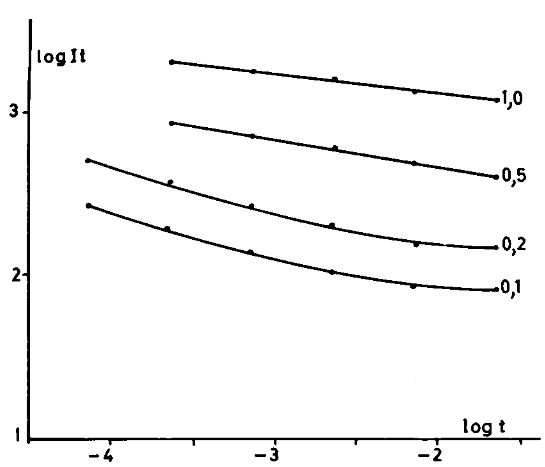

Fig. 11. AgBr suspension similar to that of Figs. 8, 9 and 10, but sulfur sensitized.

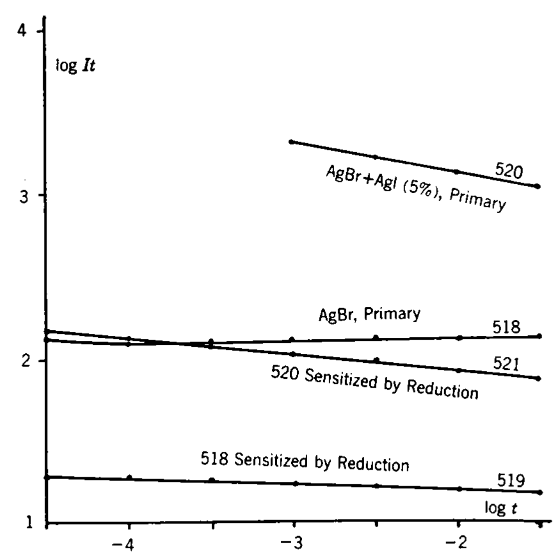

Fig. 12. Reciprocity failure curves of four AgBr emulsions.

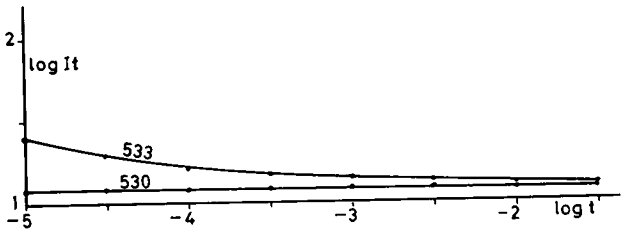

Fig. 13. Reciprocity failure curves of two gold-sensitized emulsions: (530), primary AgBr emulsion aged with KAu(SCN)$_2$; (533), AgBr + AgI (5%) emulsion similarly prepared and aged.

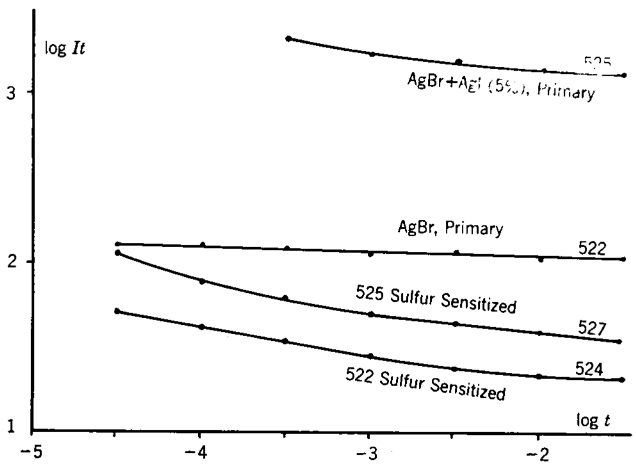

Fig. 14. The reciprocity failure curves of four emulsions.

illuminations of the primary suspension into a reciprocity failure in the direction of strong illuminations. It is to be noted, however, that the suspension sensitized by sulfuration is more sensitive (even at $t = 10^{-5}$ sec) than the primary suspension; these results show, therefore, that the sulfurizing agent sensitizes much better for exposure times $t = 10^{-2}$ sec than for exposure times $t = 10^{-5}$ sec.

Emulsion E: Figure 12 compares the reciprocity curves of four AgBr emulsions: 518 — AgBr (primary); 519 — the same, sensitized by reduction; 520 — AgBr + AgI (5%) (primary); 521 — like 520 after sensitization by reduction.

We observe the following:

(1) The addition of AgI has notably reduced the (surface) sensitivity.

(2) The two AgBr emulsions show practically no reciprocity failure.

(3) The two AgBr + AgI emulsions, especially the primary 520, show quite a considerable reciprocity failure.

Figure 13 shows a comparison of the reciprocity failure curves of the primary AgBr emulsion (530) aged with KAu(SCN)$_2$ and of the AgBr + AgI (5%) emulsion prepared and aged in precisely the same manner. The presence of AgI again produces a reciprocity failure which makes the emulsion 533 about three times less sensitive at $t = 10^{-5}$ sec, while both emulsions have the same (surface) sensitivity at $t = 10^{-2}$ sec.

In all cases studied, the addition of AgI to AgBr induced the appearance of a similar reciprocity failure (in surface development).

Since the sulfurizing sensitization of a primary AgBr emulsion, precisely as the addition of iodide to it, results in the appearance of a reciprocity failure, the logical next step was to examine the combined effect of these factors. Figure 14 shows the data for four emulsions: 522 — AgBr (primary); 524 — the same, sensitized by thiosulfate; 525 — AgBr + AgI (5%) (primary); 527 — the same, sensitized by thiosulfate.

As expected, emulsion 522 presents no reciprocity failure, while 524 does present one; the emulsions containing AgI, whether or not sensitized by sulfurization, present a reciprocity failure. Note that the reciprocity failure on the sulfurized AgBr + AgI emulsion and on the sulfurized AgBr emulsion is of the same order.

Conclusion

The preceding facts suggest that in AgBr emulsions two factors are responsible for the emergence of reciprocity failure at strong illumination: one of these is the result of the sulfurizing sensitization; the other is due to the addition of iodide. Other factors can evidently be acting in the same sense. It may be affirmed, nevertheless, that the pure AgBr emulsions of the primary type do not present any reciprocity failure at strong illuminations, at least not out to exposure times of 10^{-5} sec, as regards the latent surface image.