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THE EFFECT OF A PULSED ELECTRIC FIELD ON THE FORMATION OF A LATENT PHOTOGRAPHIC IMAGE

(Presented by Academician E. K. Zavoisky on 15 V 1968)

This paper sets forth experimental results that make it possible to propose a probable mechanism for the effect of a pulsed electric field (p.e.f.) on the process of formation of the latent photographic image in emulsion microcrystals.

The experiments were performed on emulsion layers without a support, 30 to 60 μ thick, under the single synchronous action of a p.e.f. ($E = (5 \div 10) \cdot 10^5$ V/cm, $T_{\text{p}} = 20$ μsec) and a light flash ($T_{\text{fl}} = 1$ μsec). The characteristics of the p.e.f. and of the light flash are given in work ([1]).

For the work, emulsions were synthesized with an average silver-halide microcrystal size of 0.3 μ. The crystal-size distribution curve was kept constant for the different emulsions and was monitored by measuring crystal sizes in electron-microscope photographs of single-layer preparations. At different stages of synthesis, additives were introduced that changed the character and distribution of electron traps in the crystals. Various types of experimental emulsions were tested; their composition and synthesis conditions are given in Table 1, and the experimental results are presented in Fig. 1.

Table 1

Composition of emulsions

Element	Atomic weight	Type 1, initial: atoms per Ag atom	Type 1, initial: weight in g per 1 g Ag	Type 2, initial with hyposulfite: atoms per Ag atom	Type 2, initial with hyposulfite: weight in g per 1 g Ag	Type 3, initial with gold: atoms per Ag atom	Type 3, initial with gold: weight in g per 1 g Ag	Type 4, initial with rhodium: atoms per Ag atom	Type 4, initial with rhodium: weight in g per 1 g Ag	Type 5, rhodium with gold: atoms per Ag atom	Type 5, rhodium with gold: weight in g per 1 g Ag
Ag	108	1	1	1	1	1	1	1	1	1	1
Br	79.9	0.434	0.321	0.434	0.321	0.434	0.321	0.434	0.321	0.434	0.321
Cl	35.5	0.551	0.178	0.551	0.178	0.551	0.178	0.551	0.178	0.551	0.178
I	126.9	0.0145	0.0170	0.0145	0.0170	0.0145	0.0170	0.0145	0.0170	0.0145	0.0170
S	32			$1.22\cdot 10^{-3}$	$3.62\cdot 10^{-4}$						
Rh	102.9							$4.06\cdot 10^{-6}$	$3.87\cdot 10^{-6}$	$4.06\cdot 10^{-6}$	$3.87\cdot 10^{-6}$
Au	197					$2.36\cdot 10^{-6}$	$4.3\cdot 10^{-6}$			$2.36\cdot 10^{-6}$	$4.3\cdot 10^{-6}$

Note. The elements entering into the composition of gelatin are not considered, since all emulsions were synthesized on the same low-active gelatin, whose content remained constant and equal to 68% by weight. Physical ripening: 30 min at 45°; types 4 and 5—in the presence of rhodium salts. Chemical ripening in various experiments: 0-2 hours at 45°; type 2—in the presence of hyposulfite, types 3 and 5—in the presence of gold salts.

Analysis of three series of experiments (Fig. 1a, b, c) shows that, in those cases where the efficiency of internal electron traps formed in silver-halide crystals during physical ripening differs little from the efficiency of surface traps formed during chemical ripening (emulsion of type 1), exposure in the p.e.f. does not change the photographic properties (Fig. 1a). If, during the process of chemical ripening, the emulsion (types 2 and 3) was subjected

Fig. 1. Characteristic curves of the experimental emulsions.
a —emulsion of the first type: **1** —exposure without a pulsed electric field, chemical ripening time 0 min.; **2** —the same with exposure in a pulsed electric field, $E = 1\cdot 10^6$ V/cm; **3** —exposure without a pulsed electric field, chemical ripening time 60 min.; **4** —the same with exposure in a pulsed electric field, $E = 1\cdot 10^6$ V/cm.

b –emulsion of the second type: **1** –exposure without a pulsed electric field, chemical ripening time 30 min.; **2** –the same with exposure in a pulsed electric field, $E = 7.5 \cdot 10^5$ V/cm.
c –emulsion of the third type: **1** –exposure without a pulsed electric field, chemical ripening time in the presence of gold salts 0 min.; **2** –the same with exposure in a pulsed electric field, $E = 1 \cdot 10^6$ V/cm; **3** –exposure without a pulsed electric field, chemical ripening time in the presence of gold salts 60 min.; **4** –the same with exposure in a pulsed electric field, $E = 1 \cdot 10^6$ V/cm.
d –emulsion of the fourth type: **3a** –exposure without a pulsed electric field of the original emulsion (type 1) without rhodium salts in physical ripening, chemical ripening time 60 min.; **1** –exposure without a pulsed electric field, physical ripening in the presence of rhodium salts, chemical ripening time 60 min.; **2** – the same with exposure in a pulsed electric field, $E = 6 \cdot 10^5$ V/cm.
e –emulsion of type 5: **1** –exposure without a pulsed electric field, physical ripening in the presence of rhodium salts, chemical ripening in the presence of gold salts, chemical ripening time 60 min.; **2** –the same with exposure in a pulsed electric field, $E = 1 \cdot 10^6$ V/cm.
f –comparative characteristic curves of emulsions: **1a** –exposure without a pulsed electric field of an emulsion of type 5; **2a** –the same with exposure in a pulsed electric field, $E = 1 \cdot 10^6$ V/cm; **3b** –exposure without a pulsed electric field of an emulsion of type 3, sensitized during chemical ripening with gold salts, chemical ripening time 60 min.

chemical sensitization, which changes the structure or increases the effectiveness of surface traps [(2)] in comparison with internal ones, the action of the pulsed electric field during exposure causes a certain increase in the sensitivity of the emulsion, increasing with an increase in the depth [(3)] of the surface traps in comparison with the internal ones (Fig. 1b, curve 2, and Fig. 1c, curves 2 and 4).

In the next series of experiments an emulsion was investigated (type 4) in whose microcrystals the number of internal electron traps had been increased. For this purpose, emulsification and physical ripening of the initial emulsion were carried out in the presence of rhodium chloride, the introduction of which, as shown in [(4)], in an amount of $(1 \div 18) \cdot 10^{-6}$ mole Rh per 1 mole Ag leads to a decrease in sensitivity and an increase in contrast (with the size-distribution curve of the emulsion microcrystals remaining unchanged), i.e., to the appearance of a large number of internal traps competing for the capture of photoelectrons with surface traps.

Curve 2 in Fig. 1c indicates that, in the presence of rhodium in the emulsion, the effect of the pulsed electric field is appreciably greater than in all the preceding cases.

Next, an emulsion of type 5 was subjected to the action of the pulsed electric field; its microcrystals possessed a large number of effective internal traps and the most effective of all known surface traps–gold-sensitized traps. It follows from Fig. 1d that the sensitivity of an emulsion of this type is increased by the

pulsed electric field by approximately a factor of 10.

In Fig. 1e a comparison is made of the characteristic curves of emulsions of types 3 and 5 (the latter exposed in the pulsed electric field). Comparison of the curves shows that applying the pulsed electric field during exposure of emulsions whose sensitivity had been artificially reduced by the formation of a large number of internal electron traps in the microcrystals can, under the most favorable experimental conditions, lead to reproduction of the initial characteristic curve of the emulsion, i.e., to restoration of the former sensitivity and contrast.

It should be emphasized that application of the pulsed electric field does not lead to an increase in the degree of fogging of the emulsion and does not cause breakdown.

Experiments similar to those described were carried out by us on various initial emulsions. With changes in the formulation and synthesis conditions of the initial emulsion, the degree of reduction of its sensitivity by rhodium salts and the degree of increase of its sensitivity by gold salts change, since the effectiveness, depth, and quantitative ratio of internal and surface traps change. Restoration of the photographic properties of an emulsion, in turn, depends on the strength of the pulsed electric field, on the ratio of the durations of the light flash and the field pulse, on the degree of synchronism between them, etc. However, under no experimental conditions with a single pulse did we succeed in obtaining an emulsion sensitivity and contrast greater than those of the initial emulsion. The experimental results obtained in works [5–7] do not contradict our results.

The mechanism of the increase in sensitivity under the action of the pulsed electric field appears to be as follows. A pulsed electric field, applied synchronously with exposure, shifts interstitial ions Ag^+ and the photoelectrons that arise to opposite sides of the microcrystal, in an amount proportional to the strength of the pulsed electric field. After the action of the external pulsed electric field has ended, the more mobile photoelectrons (lifetime $T_e \approx 0.3$ μs), moving toward the Ag^+ ions (duration of the ionic stage $T_i \gtrsim 1$ μs), encounter traps on their way, both internal and surface, and are captured by them, but in an amount of no more than one by each trap. The Coulomb field of the negatively charged trap attracts an interstitial ion Ag^+, which neutralizes the trap and is most reliably retained (like the electron) by a deep surface gold-sensitized trap.

trap. This trap, grown by one silver atom, becomes still more effective in capturing or even in drawing off electrons from neighboring small and shallow traps, which should first of all include internal rhodium traps.* Immediately and for some time after the removal of the pulsed electric field, the bulk of the negatively charged traps has not yet grown, awaiting the arrival of Ag^+ ions, and therefore can serve as a source of electrons (for example, because of thermal emission) for the traps that grow first of all, namely the gold-fogged traps.

If the electric field did not intervene in the formation of the latent image, then the interstitial ions—and, after a short light flash, the electrons captured by traps

—would prove to be uniformly distributed over the volume of the microcrystal. In this case there is a high probability of rapid and simultaneous neutralization of each trap by the nearest interstitial Ag^+ ion. In other words, a finely dispersed latent image arises in the microcrystal, and the sensitivity of such an emulsion will be low.

After exposure in a pulsed electric field, a redistribution of photoelectrons more favorable for deep traps takes place. In the best case, the pulsed electric field helps the surface center, in the course of the usual alternation of electronic and ionic stages, to capture successively all the photoelectrons, which corresponds to a return to the sensitivity inherent in an emulsion containing no rhodium.

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* An idea of the relative depth of traps consisting of rhodium, silver, or gold is given by data on the electron work function in the photoelectric effect for these metals (8), which indicate an increase in the work function in the stated sequence.

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

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