

The Peculiarities of an Electrolytic Reduction of Emulsion Grains

Valery Zakharov
Department of Chemistry, Moscow State University, Russia

Abstract

Common features and differences in the effect of electric current and very high electric field pulses in emulsion grains are suggested and proposed for discussion. The possibility of injection of electrons into emulsion grains is proposed as general source of all observed regularities. The present report deals with an analysis of the problem as well as giving a description of some new experiments.

Introduction

Since the early days of photography, various workers have investigated the effects of electric currents on photographic materials. Daguerre[1] himself endeavored to increase the sensitivity of his iodized metal plate by the passage of weak current through it. Banks[2] appears to have been the first actually to develop a photographic image by electrolytic action. The possibility of electric control of the photographic process, such as, for instance, control of light -sensitivity according to a "switch-on" and "switch-off" program has been reported in [3]. At later stages effects of both electric current and high voltage pulses on emulsion layers and on separate grains were studied in greater detail. *Electrolytic effect of current from low-voltage* sources have been used by Rzumkovski[4] to obtain electrically developed portrait. The development required 15 minutes at potential of few volts and current of 0.25 amperes. Zyskin[5] proposed, in 1961, the method of combining the process with electrolysis. Electrolysis of the emulsion as a method of reduction chemical sensitization was patented by "Eastman Kodak"[6] as early as 1968. The Zyskin method found application both in methods of developing emulsion layers,[7] as well as separate grains.[8] In the Moeller methods,[8] as well in all its successive modifications a 100 μm dia platinum wire is used as cathode. A silver wire with a large contact area to the light-sensitive layer is used as anode. The potential difference applied to the above electrolytic cell determined the overvoltages at which actual nucleation or development of latent image took place. It did not exceed 1V. The following noteworthy peculiarities in reduction of emulsion grains were observed in [8-11]. The current passed through the circuit only at the moment of contact between the platinum wire and the grain surface protected by a thin gelatine coating. After termination of complete reduction of the silver bromide microcrystals the platinum electrode was transformed into a silver bromide one, and the cell became symmetric. The high ohmic resistance of the circuit prevented further current flow. The amount of electrons necessary for reduction corresponded completely to the number of silver ions in the grain. Another feature of cathode reduction of emulsion grains consists in existence of critical potential of platinum electrode with respect to the silver bromide one, at which the selectivity of development of latent image is disturbed. According to [10] selective development of exposed grains takes place at potential of 260-280 mV. At higher potentials, e.g. at 400mV and higher development of all grains takes place, regardless of presence or absence of latent image specks. There remain only differences in reduction kinetics. These difference disappear at 800 mV and higher. In accordance with data[8] the time of full reduction of grains by platinum electrode equals 10 ms, which corresponds to an injection rate $3*10^{12}$ electrons per second. Such extraordinary high rate precludes the possibility of a staged development of the process.

Light-sensitivity increase in electric fields was observed by Rothstein[12] in 1960. The effect was studied by many workers.[13,14] Pulsed fields of intensities 10^5 - 10^6 V/sm were applied. An increase in light-sensitivity sets in after a certain threshold value of field pulse strength. At insufficient field strength a decrease in light-sensitivity is observed. Highest possible increase in light-sensitivity attained at exposure at maximum field strength. Further increase in field strength or in the duration of its action is accompanied by a fast intensification of fog. In the case of electrolytic reduction of grains as well as in case pulsed of field action there is a practically complete absence of "through"-conductivity. In the first case the grains are reduced through electron injection from the cathode. As soon as the reduction process is completed and silver bromide is transformed into metallic silver, the current flow in the circuit stops. Under action of pulsed fields the emulsion layer which possesses considerably higher conductivity than the plastic base plays the part of a condenser plate. This effect (i.e. speed increase) may only be observed after saturating the layer with nonabsolutized alcohol (azeotropic mixture of alcohol with water) or with alcohol-glycerol mixture. Such a treatment produces stable conductivity of emulsion layer. Under these conditions injection of charge carriers into the layer may take place. They are capable of causing processes similar to those observed in the case of electrolytic reduction grains.

Preliminary Consideration

Matejec and Moizar[15] paid special attention to the interaction between electrons and mobile ions:

$$e^- + Ag^+_0 \Leftrightarrow Ag_x \quad (1)$$

Ag_x - neutral silver atom. An important parameter in photographic process is thermodynamic activity of silver a_{Ag}, which, according to (1) is determined by the product of silver ion and electron concentrations. In the description of properties of small silver particles the effect of value and sign of electric potential of these particles has to be taken into account. A quasi-equilibrium state of a system consisting of a small particle of bulk silver can be achieved with the aid of a potential difference of definite sign of potential difference. In this case the condition of equality of chemical potentials of silver atoms in the particle and in bulk metal is satisfied:

$$\mu_{rc} = \mu_\infty \quad (2)$$

where $\mu_{rc} = \mu^0_{rc} + eU_{rc}$, $\mu_\infty = \mu^0_\infty + eU_{Ag/AgBr/Ag+}$, μ^0_{rc} and μ^0_∞ and μ_∞ - chemical potentials of silver of small particle and massive metal in presence or absence of electric field, and U_{rc} and $U_{Ag/AgBr/Ag+}$ are their electric potentials, respectively.

The chemical potentials of silver atoms can be replaced by the sum of chemical potentials of silver ions and electrons by virtue of reaction (1):

$$\mu^0_{rc} = \mu^+_{rc} + \mu^-_{rc} \qquad \mu^0_\infty = \mu^+_\infty + \mu^-_\infty \quad (3)$$

where μ^+ and μ^- are chemical potentials of mobile silver ions and electrons.

A natural condition for quasi-equilibrium of the small silver particle and the bulk is also equality of the chemical potentials of mobile silver ions capable of migrating over the emulsion grains or the bulk of the solution:

$$\mu^+_{rc} = \mu^+_\infty = \mu_{Ag+} \quad (4)$$

where μ^+_∞ and μ_{Ag+} are the chemical potentials of the silver ions in the massive electrode and in the emulsion microcrystal.

The quasi-equilibrium between a small particle or a drop and its surroundings is determined by the Gibbs-Thomson equation:

$$kT\ln P_r/P_\infty = 2\sigma V_0/r_c \quad (5)$$

where v_0 - volume of liquid phase par one molecule, P_r and P_∞ - vapour pressure over a small drop and the phase, respectively. For processes in condensed phases $P_r/P\infty$ ratio is replaced by C_r/C_∞ concentration ratio. At precise calculation, C_r/C_∞ ratio must be replaced by thermodynamic activities of a/a_∞ ratio. From (2) and (5) we obtain a modified Gibbs-Thomson equation:

$$2\sigma V_0/r_c = e\Delta U_{rc} \quad (6)$$

where $U_{rc} = kT\ln C/C_\infty$ is the electric potential difference capable of maintaining the silver clusters at quasi-equilibrium. As demonstrated by Moizar and Granzer[16] it is permissible to replace the C/C_∞ ratio by $[e]/[e]_\infty$ in the case of processes in emulsion grains. Here [e] is stationary concentration producing supersaturation, $[e]_\infty$ is the electron content at thermodynamic equilibrium.

$$U_{rc} = (kT/e)\ln[e]/[e]_\infty \quad (7)$$

For further refinement of the general picture experiments on electrolytic reduction of whole emulsion layers and not separate grains may be of considerable interest.

Experimental and Results

The dimensions of platinum electrodes were increased. The emulsion was poured on the paper base without dilution. Otherwise the method of electrolytic reduction did not undergo any essential changes. By means of preliminary illumination a latent image was obtained on part of the emulsion layer in form of strip positioned at right angeles to the direction of motion of platinum electrode.

A generalized picture of experimental results is presented on Figure 1 in form of densitogrammes obtained at different and steadily increasing relative values of negative electric potential of the platinum electrode. Figure 1 yields two critical values of platinum electrode potential with respect to anode potential. At constant displacement rate of the platinum electrode there exists a region of potential at which where is no reduction of grain even in the presence of latent image.

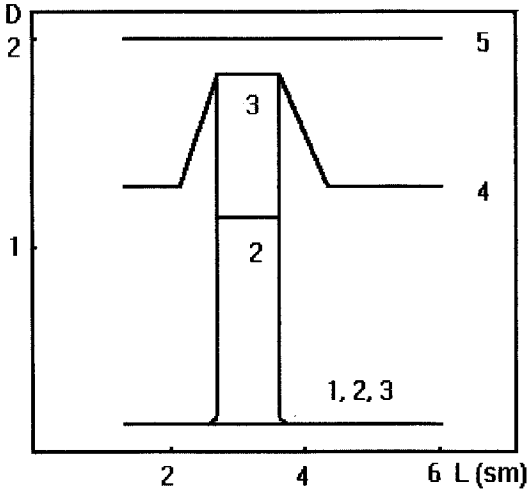

Figure 1. Effect of cathode potential on selectivity of electroreduction of grains of undiluted positive emulsion. Relative potential values: 1-0,25 (absence of reduction); 2-0,5 (onset of reduction of exposed (grains); 3-1,0 (complete and selective reduction of grains at slower rate); 5-6.0 and higher (non-selective reduction of latent image specks).

Within a certain range of potentials highly selective reduction is observed of only such grains which have previously been exposed. The second critical potential value corresponds to the metastable boundary of spontaneous nucleation of development specks. In this region there are still differences in the kinetics of reduction of exposed and non-exposed grains. At still more negative potentials of the platinum electrode the discrepancies in kinetics disappear completely. A rather important observation consists in considerable speed increase in fine-grain emulsions if the electrolytic "injection" of electrons takes place before exposure. The reduction process may develop according to two different schemes:

1. direct injection
e^- (cathode) + Ag^+_{Ag} (emulsion grain) $\Rightarrow$ Ag^x_{Ag} (8)

2. with the aid of donor-acceptor impurity
e^- (cathode) + A $\Rightarrow$ A^-
A^- (donor) + $Ag^+_{Ag} \Rightarrow$ A + Ag^x_{Ag} (9)

The results of thermodynamic analysis of these two cases coincide. For electrolytic reduction Faraday's law is valid, i.e. reduction of each silver grain requires the transition of one electron from cathode. This condition holds sufficiently strictly at small cathode displacement rates, i.e. conditions close to equilibrium. The detailed analysis of the mechanism of the phenomena applying thermodynamic approach to the theory of photographic process has been made in [17]. The device based on a low voltage electrolytic reduction of emulsion layers was patented[18] in 1993.

Conclusion

The peculiarities of electrolytic reduction of emulsion grains permit to propose an alternative mechanism of raising light sensitivity by action of high-voltage pulses. In electrolytic reduction of emulsion grains conduction currents are absent. With the aid of a "mediator" injection of electrons from platinum electrode directly into the grains takes place. This is experimentally ascertained fact. Despite the colossal divergences in applied potential differences (ca. 1 V and ca. 100 kV) a similar situation is created under pulsed field action. Injection of carriers from the surroundings into the grain becomes part of the process and, possibly, the most important one. The extremely short duration of the pulse, of order of 10^{-6} s prevents spontaneous fogging. Therefore an effect of raising light-sensitivity takes place which could not be achieved by conventional methods of sensitization and hypersensitization.

References

1. J. M. Eder, *Handbuch d. Photographie*, 3rd edition, **1**, part II, 421 (1906).
2. E. Banks, *Brit. J. Phot*., **42**, 648 (1895); ibid, **43**, 647 (1896).
3. A. L. Kartuzhanskii, *Uspehi fiz. nauk* (Rus.)**73**, 471 (1961).
4. J. Rzymkowski, *Phot. Ind*., **35**, 453 (1937); U.S. Patent 2,356,536 (1944).
5. N.M.Zyuskin, USSR Patent 135338 (1961*); Zh. nauchn. I prikl. fotogr. i kinematogr*.(Russ.) **6**, 3362 (1961).
6. J. Figueras, U.S.Patent 3,411,917 (1968).
7. D. M. Samoilovich and V. G. Tarasenkov, *Zh. nauchn. I prikl. fotogr. I kinematogr*. (Rus) **8**, 151, (1963).
8. G. Möller, *ICPS*, Moscow, sect. **AB**, 125 (1970).
9. A. B. Holland and J. R. Sawers, *Photogr. Sci*., **17**, 297(1973).
10. A. Daniel and W. F .Berg, *J. Photogr. Sci*., **23**, 131(1975).
11. R. Winsauer and W. F. Berg, *ICPS*, Rochester, 74, (1978).
12. J. Rothstein, *J. Photogr. Sci*., **3**, 255(1959); **4**, 5 (1960).
13. A. L. Kartuzhanskii, V. M. Ulanov and A. F. Yurchenko, *Phys. Stat. Sol*. (a),**75**, 669, (1983).
14. E. A. Galashin, *Zh. nauchn.i prikl. fotogr.i kinematogr.*, **32**, 68 (1987).
15. R. Matejec and E. Moizar, *Photogr. Sci. Eng*., **12**, 133(1968).
16. E. Moizar and Granzer F., *Photogr. Sci. Eng*., **26**, 1 (1982).
17. E. A. Galashin, V. N. Zakharov, *J. Inf. Rec. Mater*., **18,** 463 (1990).
18. V. N. Zakharov, N. N. Alekhin, USSR Patent 1790774 (1993).

Acknowledgements

The work described herein was supported by the Russian Foundation for Basic Research (grant 96-03- 32263a). The author also would like to thank the Netherlands Organization for Scientific Research (NWO) for financial support.