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Abstract

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ACTIVATION ENERGY OF THE THERMAL DISPERSAL OF A LATENT PHOTOGRAPHIC IMAGE

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Any modern theory of the formation of a latent photographic image includes, among others, the following two propositions: 1) in the process of growth of a latent-image center, the activation energy required for its thermal dispersal is a monotonically increasing function of the number of atoms in the center; 2) thermal stability is attained in the process of growth of the center earlier than the ability to catalyze development. The second proposition is supported by a number of experiments demonstrating the existence of catalytically still inactive, but thermally already stable, groups of Ag atoms–so-called subcenters; the first proposition (without which the second also loses its meaning) is based only on general considerations and has not been experimentally investigated for AgHal. Meanwhile, P. V. Meiklyar ([1],[2]) proposed a method based on the analysis of curves expressing the phenomenon of nonreciprocity (so-called isopacs) for photographic layers in the region of long exposure times, which in principle makes it possible to determine the number of Ag atoms in a subcenter and the activation energy of any group of atoms whose size does not exceed that of a subcenter. The results set forth below contain such data, obtained experimentally by Meiklyar' s method. However, since the method itself was in general formulated extremely briefly ([2]), and the formulas obtained were not brought to a form allowing direct comparison with experiment, we precede our data with a certain modification and supplement to the indicated method.

The phenomenon of nonreciprocity at long exposure times is caused by thermal dispersal of latent-image centers in the initial (pre-subcenter) stage of their formation, and is expressed in the fact that, for all exposure times t greater than some optimal t_0, the amount of exposure H necessary to obtain a given blackening depends on t, increasing monotonically with the latter. The minimum value $H = H_0$ evidently corresponds to $t = t_0$. If at $t = t_0$, in order to impart developability to an individual photographic-emulsion crystal, the formation in it of N_0 Ag atoms is required, then at $t > t_0$ for the same purpose $N > N_0$ atoms are required, since some of them subsequently disappear as a result of thermal dispersal. Hence, taking into account the proportionality of N and H, it follows that for all $t > t_0$ one must have $H > H_0$. According to Meiklyar, the dependence of N on t is given by the equation*

$$N - N_0 = \sum_{r=1}^{n-1} A_r \left(\frac{t}{N}\right)^r , \tag{1}$$

where

$$A_r = \gamma^r \sum_{i=1}^{r} \exp\left(-\frac{U_i}{kT}\right) \tag{2}$$

* The notation used here and below differs from the original.

(ν is the frequency of thermal vibrations, U_i is the activation energy for resorption of a center consisting of i atoms). The summation in (1) is carried out over all unstable groups of atoms; consequently, the number of atoms in a subcenter is n, since $n-1$ atoms is the largest unstable group. Equation (1), after passing from N to H, is an analytical expression for the isopaque.

For comparison with experiment it is useful also to calculate $d\lg N/d\lg t$, or, what is the same, $d\lg H/d\lg t$; this quantity gives the slope of the isopaque, since it is customary to construct the isopaque in the form $\lg H = f(\lg t)$. The complicated expression obtained from (1) can be simplified by introducing the Schwarzschild exponent $p = 1 - d\lg H/d\lg t$:

$$\frac{1}{p} = n - (n-1)\frac{N_0}{N} - (n-2)\frac{A_1 t}{N^2} - (n-3)\frac{A_2 t^2}{N^3} - \ldots - \frac{A_{n-2}t^{n-2}}{N^{n-1}}. \tag{3}$$

As $t \to \infty$, N also increases without bound. Dividing both parts of (1) by N, it is easy to see that its left-hand side is always finite, and hence t^{n-1}/N^n is finite as $t \to \infty$; consequently, $1/p \to n$. Thus n is found directly from experiment from the limiting slope of the isopaque. Usually $p \geqslant 1/2$, i.e. $n = 2$ (^{3}), and therefore the subcenter is often regarded simply as a group of two atoms. However, for low-sensitivity emulsions with a clearly pronounced decrease of contrast at large t, values of p down to 0.3-0.25 are encountered (at least for large blackenings), which correspond to values $n = 3$-4.

Equation (1) is of degree n with respect to $1/N$; although n is found from (3), to solve it one must also know the coefficients A_r and N_0. It is precisely in finding these that the main difficulty in solving (1) lies, while the quantities of interest to us are contained precisely in the coefficients A_r, and knowing them is more important than obtaining the solution. For $n = 2$ there are always two such coefficients, and to find them Meiklar (^{1}) proposed comparing isopaques obtained at two different temperatures, assuming N_0 to be temperature-independent (this was justified experimentally) and ν known ($\sim 10^{13}$ sec^{-1}). The case $n = 2$ was carried through by Meiklar to the end, and we shall not consider it. Here we shall examine the cases $n = 3$ and $n = 4$, following the same procedure.

For $n = 3$ we have:

$$1-\frac{N_0}{N}=\frac{A_1t}{N^2}+\frac{A_2t^2}{N^3}; \tag{4}$$

$$\frac{1}{p}=3-2\frac{N_0}{N}-\frac{A_1t}{N^2}, \tag{5}$$

where

$$A_1=\nu\exp\left(-\frac{U_1}{kT}\right),\quad A_2=\nu^2\exp\left(-\frac{U_1+U_2}{kT}\right).$$

Combining (4) and (5), we obtain

$$\frac{A_2t^2}{N^3}-\frac{N_0}{N}+2-\frac{1}{p}=0. \tag{6}$$

At the point of the isopaque for which $p=1/2$, from (6) we immediately have

$$\frac{N}{N_0}=\frac{H}{H_0}=t\sqrt{\frac{A_2}{N_0^3}}. \tag{7}$$

From the experimental values of t and H/H_0 at the points $p=1/2$ for temperatures T' and T'', we shall successively find A_2'/A_2, U_1+U_2, A_1' and A_2', N_0, after which from (5), replacing N by N_0H/H_0, we shall find A_1 and U_1; now having the values of U_1 and U_1+U_2, we determine U_2.

Similarly, one can proceed in the case $n=4$. Here

$$1-\frac{N_0}{N}=\frac{A_1t}{N^2}+\frac{A_2t^2}{N^3}+\frac{A_3t^3}{N^4}; \tag{8}$$

$$\frac{1}{p}=4-3\frac{N_0}{N}-2\frac{A_1t}{N^2}-\frac{A_2t^2}{N^3}, \tag{9}$$

where $A_3=\nu^3\exp\left(-\frac{U_1+U_2+U_3}{kT}\right)$; A_1 and A_2 are as before. From (8) and (9) we obtain

$$\frac{A_3t^3}{N^4}-\frac{A_1t}{N^2}-2\frac{N_0}{N}+3-\frac{1}{p}=0. \tag{10}$$

Finding the point of the isopaque at which

$$\frac{1}{p}+2\frac{H_0}{H}=3$$

Fig. 1

Figure 1: Fig. 1

(since H_0/H is small there, p is close to 1/3), we obtain, after minor transformations,

$$\frac{N}{N_0} = \frac{H}{H_0} = \frac{t}{N_0}\sqrt{\frac{A_3}{A_1}}. \tag{11}$$

Having, as before, isopaques at two temperatures T' and T'', and noting that

$$\frac{A_3}{A_1} = \nu^2 \exp\left(-\frac{U_2 + U_3}{kT}\right),$$

we can successively find

$$\frac{A_3''}{A_1''}\bigg/\frac{A_3'}{A_1'}, \quad U_2 + U_3, \quad A_3''/A_1'' \text{ and } A_3'/A_1', \quad N_0;$$

then from (10) we find A_3, A_1, and U_1, and from (9) we find A_2 and U_2, after which we also determine U_3. This scheme for the successive determination of all the quantities of interest to us is, apparently, the simplest possible.

Fig. 1. 1–0°; 2–20°; 3–40°; a–$D < 0.1$;
b–$D \sim 0.6$-0.8; v–$D \sim 1.5$-1.8

The object of the experimental study was a fine-grained silver-bromide photographic emulsion which had not undergone secondary ripening. Plates with the emulsion under study were exposed for times from 1 to 10^4 sec. (occasionally 10^5 sec.) through a step wedge at temperatures +40, +20°, and in a number of cases 0°; details of the procedure have been described earlier ([4]). Development was carried out in an amidol developer by the dry two-temperature method adopted in nuclear physics. After measuring the blackenings and constructing isopaques for several values of the blackening density D, it turned out that the limiting slope 1/2 (p is also equal to 1/2, $n = 2$) occurs only near the threshold of blackening ($D < 0.1$); the limiting slope 2/3 ($p = 1/3$, $n = 3$) corresponds to $D \sim 0.6$-0.8, and at sufficiently large D (~ 1.5-1.8) the limiting slope reaches 3/4 ($p = 1/4$, $n = 4$) owing to the fall of contrast at large t. Isopaques for the three indicated values of D are shown in Fig. 1. Their analysis on the basis of formulas (1)–(3) and the formulas (4)–(11) following from them led to the results summarized in Table 1.

Table 1, especially its last column, clearly shows a monotonic increase of U_i with i. This increase is apparently slower than linear and, one may think, should tend toward saturation at large i; indeed, for a large center, changing it by one or even several Ag atoms does not affect its properties, as follows from a number of indirect experimental data (for example, (^{5})).

Another important result in Table 1 appears to us to be the approximately identical activation energy in all cases where the Ag particle is "pre-subcenter," i.e., where it lacks only one atom for stability (U_1 at $n = 2$, U_2 at $n = 3$, U_3 at $n = 4$). Consequently, the stability of a center is determined by the attainment of some definite value of the activation energy, regardless of how many Ag atoms were required for this. Differences in the number of atoms necessary to create a subcenter are usually associated with the effectiveness of sites of concentration of Ag sensitivity centers in emulsion crystals. Therefore, the effectiveness of a sensitivity center, as the data presented show, should be understood as the depth of the corresponding energy "trap."

Table 1

	$n = 2$	$n = 3$	$n = 4$
U_1, eV	0.84 ± 0.02	0.69 ± 0.02	0.6 ± 0.03
U_2, eV	–	0.85 ± 0.02	0.79 ± 0.03
U_3, eV	–	–	0.88 ± 0.03
N_0 Ag atoms	13 ± 1.5	20 ± 3	30 ± 5

Differences in the effectiveness of sensitivity centers in individual groups of emulsion crystals are also evident from the last line of Table 1, where they are expressed in another way: the more difficult it is for the latent image to form, the more Ag atoms are needed for the image to attain the critical size sufficient for the subsequent catalysis of development. The change of N_0 with n, and hence also with D in Table 1, also shows that the aggregate of crystals forming large blackenings is, on average, less sensitive than that forming small blackenings, as is customarily assumed in photography.

The following remark must be made. In the calculations we assumed $\nu \sim 10^{13}$. However, even if one takes $\nu \sim 10^{11}$ (^{6}), such a decrease in ν will lead only to a decrease of each exponential factor in (2) by 2 orders of magnitude, and all the energies U_i will thereby decrease by the same amount, ~ 0.1 eV, which in no way affects the conclusions drawn above. The comparatively weak temperature dependence of ν (^{7}) is also of no importance, since it is described by a Boltzmann-type factor with an activation energy much smaller than U_i.

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