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On the Induction Period of Photographic Chemical Development

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In continuance of studies reported in the previous paper, the temperature dependence of photographic chemical development, especially of induction period of development in this case, was studied. Use was made of some typical developers and a sort of dry plate, in which considerable silver iodide was contained.

Against expectation, a smaller temperature coefficient was got in case of the use of hydroquinone developer than of metol developer.

From this result, a few considerations for the mechanism of chemical development were stated.

§ 1. Introduction

In the previous paper,[1] the temperature dependence of coagulation of image was measured. In that paper, an interesting fact, although it was not the most important result in it, was indicated: the induction period of chemical development grows as the content of silver iodide in emulsion increases. Practically, even with simple metol developer, comparatively long induction period appeared in case of the use of a plate in which silver iodide was contained to the amount of 40 Mol %. From this result, one reason why the velocity of development is small in case of the use of silver iodide emulsion, although the ionic conductivity of silver iodide is greater than that of silver bromide, may be explained even from MOTT's point of view.[2][3]

However, in this case, apart from this problem, the author intended to apply this result to further research.

With pure silver bromide plate, or commercial dry plate, in which silver iodide is contained to about 2 Mol %, and metol developer, the induction period observed in the process of development is very small and it is scarecly possible to measure its value quantitatively. So, wanting at least semiquantitative data of in-

duction period with metol developer, the most typical developer, one must use special plates.

Employing the above-described plate, simple experimental research on temperature dependence of induction periods was done with a few popular developers in the present case.

§ 2. Induction Period of Chemical Development

As shown in Fig. 4. in the previous paper, the image begin to coagulate after a certain developing duration when hydroquinone developer is used. This duration is called induction period and its value is determined by the sort of developer and emulsion used. The well-known schematic representation of induction periods using various developers is shown in Fig. 1.

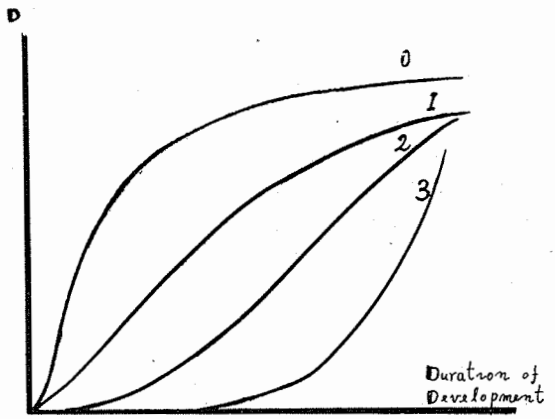

Fig. 1. Characteristic curve of development using various developers. Numbers in graph indicate the quantities of charges of developer ions.

The atomic theory for existence of the induction period has been proposed by many authors.[4)5)6)7)8)]

T. H. JAMES, who also offered an interesting consideration for the mechanism of image coagulation,[9)] noticed the relation between the induction period and the quantity of negative charge of developer ion in dissociated state.

He wrote as following:

When silver halide grains in emulsions come in contact with the developer solutions, their surfaces generally are charged up

negatively, and then the negative ions of developers in dissociated state cannot easily draw near the surfaces of silver halide grains. And if the induction period appears on account of above reason, it must grow as the quantity of charge of developer ion in dissociated state increases. There are, in fact, such relation.

His theory seems certainly to be important in explanation of the experimental results. And it is also well known when the colloidal silver halide grains come in contact with the water, their surfaces are generally charged up negatively.[10] In addition, as for the photographic emulsions, one must not forget the existence of gelatins, which perhaps effects the heights of charged barriers.[11]

However, JAMES' theory is still qualitative, and insufficient to prove that induction period can be practically determined by the quantity of charge of developer ion alone, but not the factor which was introduced by, for example, GURNEY and MOTT.

Now consider the height of potential barrier, at surface of a grain, U. Of course the height discussed in the practical case is the average one for all grains. The author assume it is determined by the repulsive force due to the negative charge on surface and the adsorption force due to latent image, and the induction period T_v of development is determined by the thirmal energy of developer ion and this potential barrier as follows;

$$T_v = C e^{\frac{U}{RT}} \qquad (1)$$

where C is a constant.

So from the above formula, U for a developing system possesing the great induction period is greater than U for a system having small induction period.

Up to this time, the induction periods of chemical development have been measured in various cases,[12] but as for these temperature coefficient there are perhaps few data. Then, using special experimental dry plate and a few popular developers, temperature coefficients was measured to check the above relation.

§ 3. Experimental Method

The measurement of induction period, although it seems to be easy, may be very difficult. There is perhaps no good method to

measure its correct value, but the value having error by a few percent can be easily observed, for example, from the characteristic curve of development. In this case, the more simple measurement, direct measurement of appearence of image using the method of trial and error, was employed. The value obtained by this simple method coincides very well with one obtained for the characteristic curve of developmeni.

The details of other experiments, exposure and fixing etc., are the same as reported in the previous paper.

The conditions of exposure in each case are neglected.

§ 4. Experimental Results

At first, the temperature dependence of induction periods was measured using pure silver bromide emulsion and metol developers in which KBr is contained in various proportions. It is well known that as the amount of bromide ions in developer solutions increases, the value of induction period grows, because bromine ions adsorp on surfaces of silver halide grains and then the heights of charged barriers on surfaces are increased. So the value of U for developer,

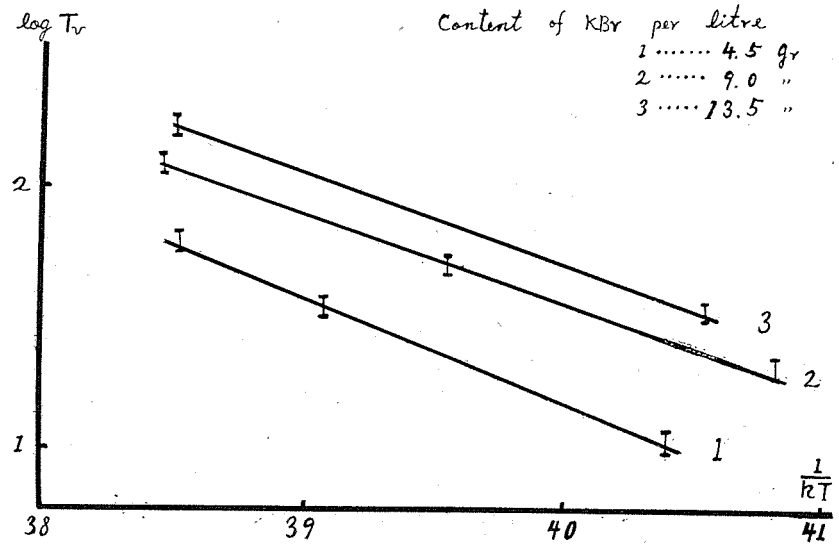

Fig. 2. The relation between the induction periods and temperatures using metol developers, in which KBr is contained in various proportions, and pure silver bromide emulsions.

in which a great amount of KBr is contained, calculated from (1) is perhaps greater than U for developer in which there is a small amount of KBr.

The experimental results are graphed in Fig. 2.

Certainly, the value of T_v grows as the content of KBr increases, but not that of U. So a conclusion is deduced as below, if the qualitative correct results, at least, are obtained even with this simple method:

"Charge effect of developer is perhaps important at the initial step of development, but also other factors will be contained in the term of T_v."

Unfortunately, the variation of the height of this charged barrier with the variation of bromine ion concentration in solution is not clear,* then discussions in this case are persistently qualitative.

Next, using the emulsion in which silver iodide is contained by 40 Mol%, the temperature dependence of the induction periods was measured in the cases of the use of simple metol developer and simple hydroquinone developer.

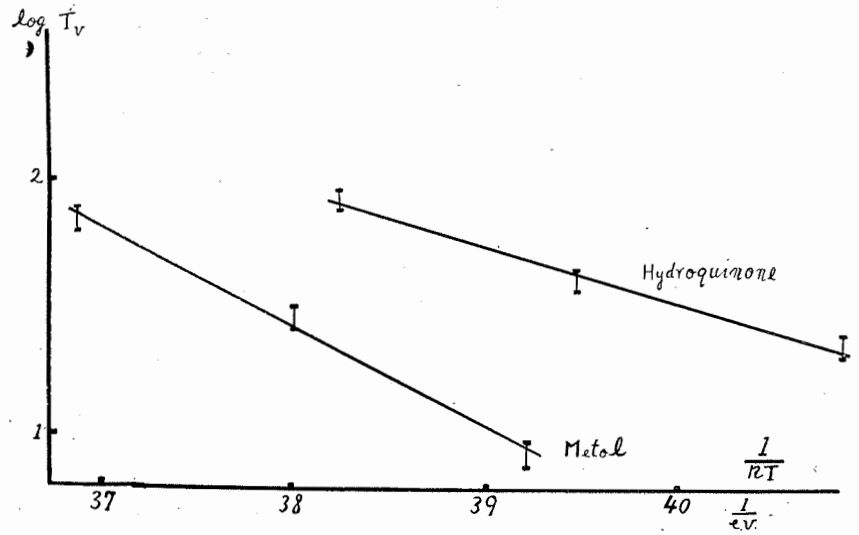

Fig. 3. The relation between the induction periods and the temperature using metol and hydroquinone developer and plate in which silver iodide is contained by 40 Mol %.

* The variations of ζ-potential on surfaces of grains are known, but not that of heights of barriers, because there are few knowledge as for the absorption force due to latent image.

TABLE 1.

The relation between the induction period and temperature using simple metol developer and simple hydroquinone developer.

	Temperature	Induction period
Metol *	4.5 °C	70±10 sec
	12.2	30± 5
	21.1	8± 3
Hydroquinone **	14.0	80±10
	23.1	40±10
	21.1	25± 5

The expectation in this case is that U for hydroquinone developer is perhaps greater than U for metol developer, because charge effect for the former is greater than that for the latter.

The results are indicated in Fig. 3 and Table 1.

Against expectation from the theory above described U for hydroquinone developer is not, greater than U for metol developer.

§5. Discussions

It is well known that the value of induction periods measured by the general method is affected by some extra terms: e.a., diffusion of developer ions through the gelatins and coagulation of image till the visible one is formed. However, the value of these factors and also the contributions of these terms to the temperature dependence are perhaps very small. Then the difference between the cases of the use of various developers may be considered to indicate the true difference of induction periods. So discussing the results stated in §4, the following conclusion is reached.

"Although the induction periods appear partly on account of coulomb repulsion between charged barrier on surface of grain and

* Metol 3.4 gr, Na_2SO_3 30 gr
Na_2CO_3 30 gr, Water 600 c.c.

** Hydroquinone 2.2 gr, Na_2SO_3 30 gr
Na_2CO_3 30 gr, Water 600 c.c.

developer ion as stated by JAMES, other important factors must be, also, contained in it."

The author can not now state, from this simple consideration, the nature of these factors, but are inclined to think that it may be important to take up the electronic structure of adsorped developer ions as these factors.

§ 6. Final Remarks

The author extend thanks to Prof. FURUICHI who led him through this work and Mr. E. MIZUKI who kindly gave him the experimental dry plates used in this experiment.

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