a. Unsaturated cells containing the sulfates of lithium, magnesium and cadmium have been studied, and the observations indicate:

(1) That their electromotive force approximately equals that of the corresponding saturated cells.

(2) That these cells are equally unsatisfactory.

(3) That the erratic values of the saturated cells are probably not, therefore, the result of the coexistence in the cell of the anhydrous sulfate and a hydrate or of different hydrates, as has been noted in certain Clark cells.

b. Evidence was sought, by means of analytical, microscopic, and thermometric methods, which would indicate whether the unsatisfactory results might be caused by the formation of double salts in the cells. The indications were:

(1) That analytically, there is evidence for the formation of only one double salt, potassium lead sulfate.

(2) That microscopically, no conclusions of value are possible.

(3) That thermometrically, the evidence points to the formation of only one double salt, potassium lead sulfate.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY. NO. 84.]

CHEMICAL INDUCTION IN PHOTOGRAPHIC DEVELOPMENT.
I. INDUCTION AND THE WATKINS FACTOR.

BY S. E. SHEPPARD AND G. MEYER.

Received December 20, 1919.

In previous investigations on the theory of development[1] it was shown that the early stage of development is subject to induction effects, variable from one developer to another, and in each case a function of the bromide concentration.

In particular it was shown that the action of bromide as a photographic restrainer consisted primarily in extending the induction period, or delaying the initial precipitation of silver; equations for the velocity of development taking account of the initial retardation were developed. It was pointed out that while this initial induction is greatly extended by bromide that it exists in the absence of bromide, particularly in the case of hydroquinone.[2] With this developer it becomes more marked on lowering the temperature.

In general, the induction is greater the less the reduction potential of the developer. The reduction potential of a developer was defined from

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[1] S. E. Sheppard, *J. Chem. Soc.*, 87, 1312 (1905).

[2] S. E. Sheppard, *ibid.*, 89, 530 (1906).

the equation for reaction and free energy; taking as the general equation for the chemical change in development,

$$Ag^+ + R^{--} \rightleftharpoons Ag + R^-,$$

then the free energy of the reaction is given to a first approximation by the expression (where [ ] signifies concentration).

$$E = RT \log \frac{[Ag^+]\,[R^{--}]}{[Ag]\,[R^-]}$$

We can imagine this separated into $RT \log \frac{[Ag^+]}{[Ag]}$, which may be termed the self-reduction potential of the silver ion[1] and $RT \log \frac{[R^{--}]}{[R^-]}$, the reduction potential of the developer. It is evident that the (initial) energy of development will be greater, the higher $[Ag^+]$, concentration of silver ion, the lower [met. Ag], concentration of metallic silver. The latter is less, as degree of supersaturation, in the presence of a nucleus, such as the latent image affords; and the supersaturation will be less the smaller the nucleus.[2] Similarly, for the reducing agent, the further the reaction phase $R^{--} \longrightarrow R^-$ can go, the greater the reducing energy and the more bromide will be necessary to restrain it.

The Watkins Factor.

The Watkins factorial method of development was introduced by Mr. Alfred Watkins[3] in 1894. He found that the time from the pouring on of the developer till the first appearance of the image stands in a constant ratio to the time of development for a given constant density. The Watkins multiplying factor is the quotient of the time of development for this constant density (or constant Hurter and Driffield development factor, γ). The Watkins factor, while showing certain variations for one and the same reducing agent, according to the composition and concentration of the bath, differs very considerably from one reducing agent to another.

The foregoing analysis of the energy factors in development explains why on the whole high reduction potential developers have high Watkins factors and small induction periods. The explanation put forward by Kingdon[4] that different reducers require different *critical concentrations* to initiate reduction, as accounting for differences in the Watkins

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[1] Representing the reaction scheme $Ag^+ + \theta \longrightarrow Ag$ met. or the affinity for electrons, in other words, its position in the electrochemical series; inversely of course, its oxidation potential as oxidizer.

[2] Nuclei below a certain magnitude will have a higher solubility.

[3] See A. Watkins, "Manual of Photography." 4th Ed. Chicago, Burke and James. 1908.

[4] *Phot. J.*, 48 (N. S. 42), 270 (1918).

factor, is obviously contained in this analysis; the *critical concentration* hypothesis is, however, incomplete, inasmuch as it does not take into account other factors which the free energy theory does, as for example, the influence of bromide. It is then of considerable interest for the theory of development that it is possible to alter the Watkins factor for certain developers in the opposite sense to that effected by bromide. The agent we have used for this is a soluble iodide, *e. g.*, potassium iodide in very small concentration. The peculiar "accelerating" effect of such iodides on development was first observed by A. Lainer.[1]

Experimental.

The greater number of our experiments were made with a pure silver bromide emulsion. The plates were exposed in an H. & D. type sensitometer and developed under constant temperature conditions. The value taken for the Watkins factor is in general more or less arbitrary, partly from the variable personal element in estimating the "time of appearance," partly from the absence of a fixed convention as to the development factor. The essential point, for the theory of development, does not consist in the absolute values of the Watkins factor, but in this fact that if we take the ratios of the time for some very low constant contrast, *e. g.* (time of appearance, t_a) to the time to develop a definite high constant contrast, *e. g.*, $\gamma = 1.00$) this ratio $t_\gamma = 1/t_a = W$, is characteristic of the developer, but varies widely from one developer to another. For our present work we have taken as Watkins factor $t_\gamma = 0.8/t_a = W$ and obtained the following results:

Concentration of Potassium Iodide 0.100 N = 0.0017%.

Treatment.	Reducer.	Temperature. ° C.	Concentration.	W.	Effect on W.
Pretreated	Elon[a]	18	0.5	(30)	×1
		..	0.33	....	×1
		..	0.25	....	×1
Pretreated	Glycin[b]	18	1.0	(16)	×2.2
Pretreated	Hydroquinone Caustic	18	....	....	×5 to 6

[a] *Elon* is methyl *p*-amidophenol sulfate Elon Developer: Elon, 5 g.; sod. sulfite, 75 g.; sod. carbonate, 25 g.; water, 1000 cc.

[b] *Glycin* is *p*-phenylamido-acetic acid. Glycin developer: Glycin, 60 g.; sod. sulfate, 120 g.; sod. carbonate, 165 g.; pot. carbonate, 165 g.; water, 1000 cc.

It appears that the "accelerating" effect of very dilute potassium iodide is practically absent with developers such as *elon*, having a high reduction potential and a large Watkins factor, while it becomes very marked with *hydroquinone*, which has a low reduction potential and a small Watkins factor. With the developers above, after a short initial stage, γ is practically unaltered by iodide. With hydroquinone carbonate, however,

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[1] A. Lainer, *Phot. Korr.*, 28, 475 (1891); "Eder's Handbuch d. Photographie," 5th Ed., III, p. 463.

the whole development course is changed, particularly at low temperature, as shown by the following curves and data:

Development with Hydroquinone Carbonate.
Temperature, 8°.

t_a. Seconds.		Time of development. Minutes.		γ[a].		log i.	
Treated.	Untreated.	Treated.	Untreated.	Treated.	Untreated.	Treated.	Untreated.
6	30	1	1	0.31	0.07	1.05	1.24
6	28	2	2	0.61	0.34	0.90	0.90
6	30	4	4	1.12	0.96	0.88	0.84

Watkins factor: Untreated 7; treated 28.

[a] γ is the slope of the D — : log E (density: $\log_{10}$ exposure) curve, log i is the intersection of the straight line portion with the abscissa.

It will be seen that while the hydroquinone carbonate developer at low temperature has a very marked induction, this is largely wiped out by 0.0001 N potassium iodide solution, giving in fact a developer of quite reasonable developing energy.

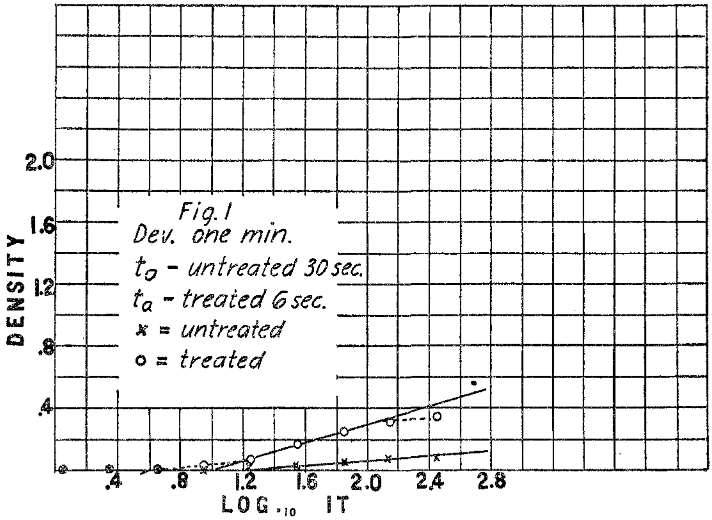

Fig. 1.—Hydroquinone carbonate at 8°. KI placed in developer.

Concentration of Potassium Iodide.

The influence of the concentration of the potassium iodide on the initial development energy with hydroquinone is shown in the accompanying curve. It will be seen that over a certain range the effect is at a maximum and then declines rapidly, till permanent restraint on development is brought about.

This latter effect is what we should expect since the iodide reacts with silver bromide forming the less soluble and less reducible silver iodide.

Nature of the Iodide Acceleration.

What is the explanation of the peculiar acceleration at low concentrations? Since the effect can be produced by preliminary bathing with weak iodide solution followed by thorough washing, it is evidently connected with the fixation of small amounts of silver iodide in the silver bromide grains, and not due to any action of the potassium iodide on the developer. The only explanation so far proposed is due to Lüppo-Cramer.[1] He supposes that in the conversion of a small fraction of the silver bromide molecules per grain into silver iodide that the halide grain is partly disintegrated or dispersed. The silver nucleus due to exposure is supposed by this to become more effective in accelerating reduction. This hypothesis of "unpeeling" the nucleus (*keimblosslegung*) has always appeared very artificial and forced, but has been repeatedly reaffirmed by its author.[2]

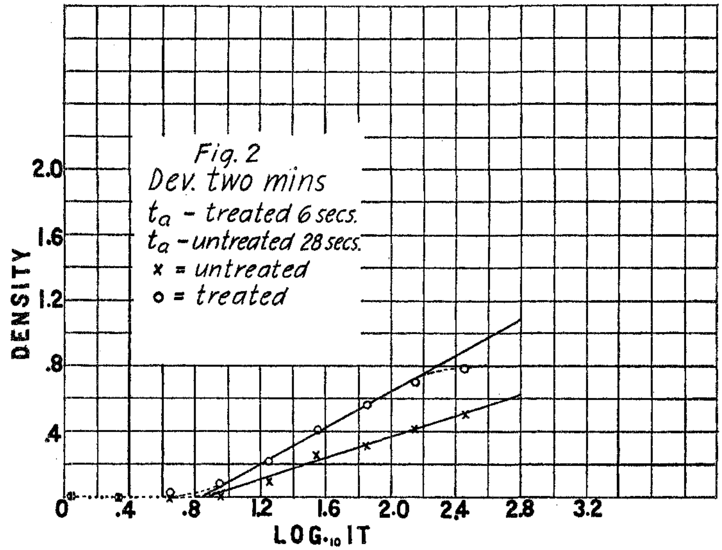

Fig. 2.—Hydroquinone carbonate at 8°. KI placed in developer.

While not readily susceptible of proof or disproof, it does not appear to line up readily with the data brought forward here, *i. e.*, with the *quantitative differences* in the iodide effect between one developer and another. In particular, the absence of an effect with ferrous oxalate appears inexplicable. It does, however, appear that an alternative hypothesis is possible of considerable higher probability. In a recent letter to the *Photographic Journal*[3] it was suggested by one of us that an important phase in development consists in the formation of an intermediate com-

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[1] *Phot. Korr.*, 49, 262 (1912); *ibid.*, 310 *et seq.*

[2] Cf. *Phot. Korr.*, 1912 and later.

[3] *Phot. J.*, 59, 136 (1919).

plex between the silver halide and the reducer, and that this unstable intermediate complex undergoes internal decomposition to metallic silver, more or less colloidal, and adsorbed to residual halide, plus discharged oxidized reducer and bromide ions. Now it appears to us that such complex formation at the surface of the silver halide grains is in line with the behavior of potassium iodide. It is well known that silver iodide has a high mordanting action for a considerable number of dyes.[1]

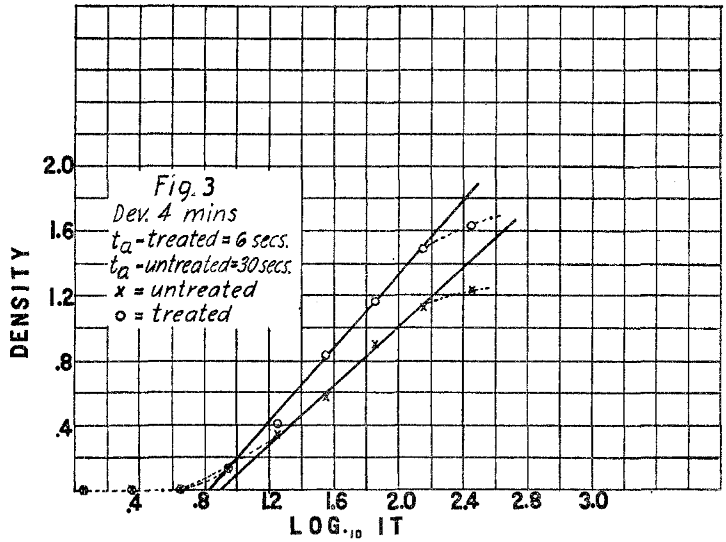

Fig. 3.—Hydroquinone carbonate at 8°. KI placed in developer.

Experiments show that either precipitated silver bromide or silver bromide emulsion acquires greatly increased dye absorption power after a preliminary treatment with dilute potassium iodide solution. On varying the concentration of potassium iodide the vanishing point, *i. e.*, the lowest concentration at which a difference in absorption could be observed between untreated and treated silver bromide is not so low as for its action on development, but this was not to be expected, since development is an extremely sensitive reaction. The results obtained are shown in the following:

Adsorption of Dye (Safranine) on Precipitated Silver Bromide.

Conc. potassium iodide solution. *N*	Excess for treated over untreated.
0.01	Strong excess
0.002	Marked excess
0.001	Definite measurable excess
0.0005	No noticeable difference

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[1] Cf. A. Traube, *Eder's Jahrb.*, 21, 103 (1907).

In these experiments 9 g. of precipitated silver bromide was first treated with 100 cc. of the potassium iodide solution, then with 50 cc. of 1 : 20,000 dye solution, the residual strength of dye in the solution being compared colorimetrically with a blank on untreated silver bromide.

Nature of the Complex Formation.

Supposing complex formation between the silver halide and the developer to be an essential preliminary to development, then this may be viewed in more than one way. First, it may be regarded as a simple excess surface concentration or *adsorption*, not necessarily involving chemical combination with the silver halide. The view that such adsorption plays an important part in development has already been expressed by W. D. Bancroft. In this case, adsorption would act chiefly by increasing the local concentration of reducer. If, however, Langmuir's[1] view is correct, that all adsorption is due to chemical (valence) forces then the complex formation will consist essentially in actual chemical combination of the surface silver halide molecules with molecules of the reducer, the valences of the surface molecules of the solid halide being less saturated than those of the interior. The nature of this combination cannot be indicated definitely at present. Thus it might be a combination primarily between the silver cation and the reducer anion, forming a salt-like body, like silver erythrosinate; this body then breaking down in the presence of a nucleus for silver. An example of this in homogeneous solution is shown in the case of silver sulfite. If this is redissolved in excess of sodium sulfite, the

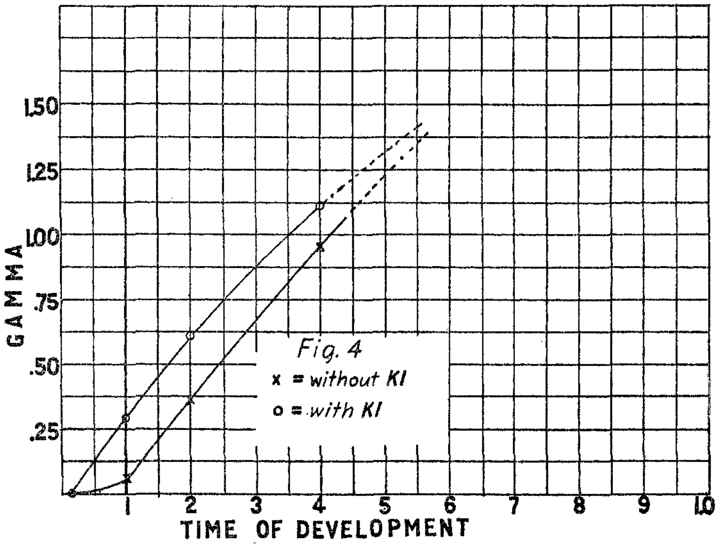

Fig. 4.—Hydroquinone carbonate at 8°. KI placed in developer.

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[1] This Journal, 38, 2221 (1916).

complex silver sulfite anion is comparatively stable at temperatures below 60°. Above this, decomposition, with precipitation of metallic silver, rapidly takes place. If now colloid silver be added to the stable solutions at lower temperatures, decomposition is at once set up and continues rapidly. The colloidal silver behaves here like the latent image in development. It is, however, equally possible that the complex formation is between the un-ionized free base of the organic reducer and the silver halide, forming a stable complex which, however, in presence of alkali (hydroxyl ions) undergoes rearrangement, *viz.*, pseudo-acid formation, salt formation, and ionization. The actual outcome would be then the same as in the former case.

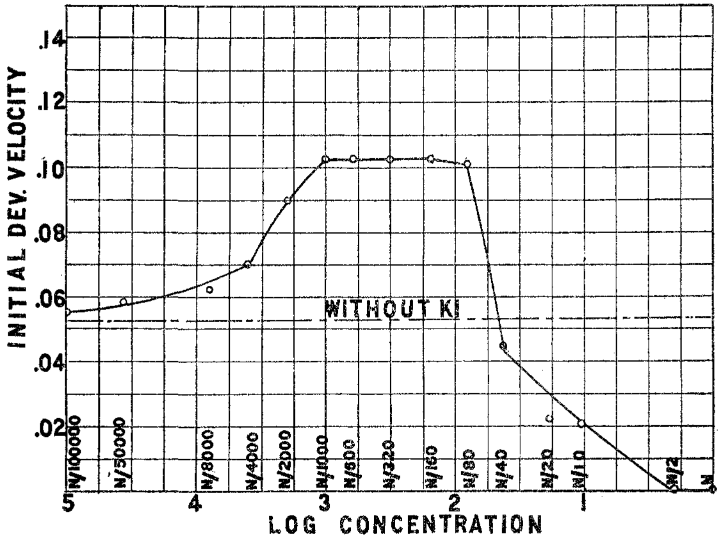


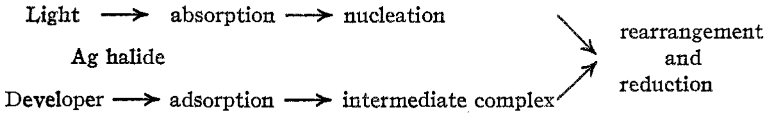
Fig. 5.

The fact that the mordanting action of silver iodide is most strongly exerted on basic dyes[1] would favor this interpretation. However, the semi-acid dyes of the phthalein group are also strongly adsorbed.

In any case, the essential matter would be the formation of an intermediate combination, in the circuit of which reaction would take place, with discharge of silver, and other oxidation products.

Relation to Silver Grain of Image.

The modification proposed in the theory of development regarding



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[1] Practically all organic reducers contain chromogenic groups, and also the auxochromes, —OH and —NH_2.

as essential steps does not contradict the previous theory, but amplifies it on two important points. First, it makes the silver halide grain more emphatically the actual seat of the reaction. It has been suggested by R. Liesegang and Lüppo-Cramer[1] that weak and strong developers in general differ essentially in that the former tend to reduce only the surface of the grain, giving an image of feeble density, usually fine grained and warm toned (ferrous citrate with silver bromide emulsions is a good example), while the latter reduce the whole of the grain, giving more coarse-grained, black-silver image. This effect of the energy of the developer on the dispersity of the image is undoubtedly real, and probably plays a considerable part in the difference of resolving power with different developers.[2]

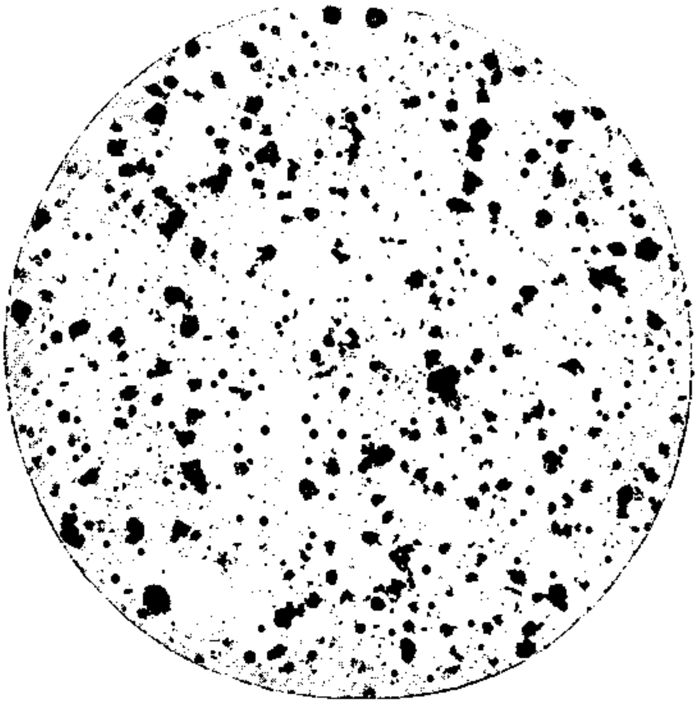

Fig. 6.—Photograph of fog caused by dil. potassium iodide solution. Mag. 600.

If adsorption of the organic reducer is correlated with its reduction potential, increasing with the latter, Bancroft's theory[3] that adsorption favors peptization of the solid phase, or adsorbent, indicates a preliminary reason for the change of dispersity of the image with energy of the reducer. Or, again, if adsorption involve formation of an intermediate complex, interfacial to the halide grain and the solution, the lability of this will depend upon the reduction potential of the reducer. This involves a greater velocity of decomposition of the complex, higher dispersity of the silver reduced, and greater mechanical strain on the silver halide

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[1] *Kolloid-Z.*, 9, 290 (1911).

[2] K. Huse, "Photographic Resolving Power," *J. Am. Optical Soc.*, 1, 119 (1918).

[3] W. D. Bancroft, "Outline of Colloid Chemistry," *J. Franklin Inst.*, 185, 376 (1918).

grain attacked. The general scheme of development which suggests itself from these considerations at this stage may be outlined as follows, bringing out the essential colloid chemical factors of the process:

Dynamics of Development.

The scheme given is only intended to roughly indicate the interaction of physical and chemical factors.

In particular, while the relation between diffusion of the developer and chemical reactivity determines the "penetration" coefficient, the relation of the "adsorption" to the chemical constitution and reactivity apparently determines the "dispersity" of the image, *i. e.*, an influence of the developer on the grain of the image.

		Remark.
a.	Swelling of gelatine film.	The swelling increases the total diffusion path, but lowers the resistance.
b.	Diffusion of developer solution.	Diffusivity increases on either side of neutral point.
c.	Adsorption of reducer to silver halide grains.	

↓	↓	↓
Weak, gives grain surface development.	Strong, volume development	
(Pectization) ⟶	(Peptization) ⟶	(Solution)
Weak colored image, fine grain.	Strong black image, coarse grain.	"Physical" development, strong, somewhat colored image, fine grain.
Example.	*Example.*	*Example.*
Ferrous citrate; acid pyrogallol.	Normal developers.	*p*-Phenylene - diamine, heavily bromided developers; D. O. P. developers with chlorobromide emulsions.

Actually, of course, these separately indicated phases of the process overlap and interact. Further, we have only noted here the *direct*, as distinguished from the *reversing* factors of development. The complications involved in the pure chemical reactions, and the regressive effects consequent on resorption of reaction products, while already noticed in part, require much further analysis.

Direct proof of adsorption of organic developers to silver halides under development conditions is difficult owing to the ensuing reactions of decomposition. Experiments to this end are in progress; meanwhile the foregoing arguments from the parallel case with dyes and from the internal evidence are submitted. It is probable that the restraining effect of pyrogallic acid in high concentrations is closely connected with the foregoing considerations.

The extension of the action of potassium iodide to physical developers, as noted by Lüppo-Cramer, is equally in agreement with the view suggested here, although complicated by the facts noted in the next section.

Fogging Action of Iodide.

With most of the developers tried, working with pure silver bromide plates, including hydroquinone at low temperatures, all strengths of potassium iodide from 0.0001 N to 0.01 N gave on short contact with the emulsion and subsequent washing pronounced fog, consisting of black-silver grains silmilar to those developed from exposure to light. This fogging action is not primarily connected with acceleration of development, since it was observed with ferrous oxalate, where practically no "development acceleration" occurs. As it appeared possible that the trace of silver iodide formed was acting as a nucleus[1] the following experiment was made. A silver-bromide plate was spotted with 0.0001 N potassium iodide solution, fixed in hypo and washed. These spots were then developed in a pyro-citric-acid-silver developer, when they developed up a strong image (see Fig. 6). The photomicrograph shows that the image is comparatively coarsely grained, quite different from the grainless stains frequently obtained on physical development. Hence, it appears probable that the iodide fog is a nucleus infection. It appears considerably more variable than the development acceleration, and less evident with bromo-iodide emulsions. The part played by this in connection with actual development acceleration is being taken up in connection with other development "promoters," as thiosulfate, potassium ferrocyanide, and thiocarbamide.

Lüppo-Cramer[2] notes that "fog is accelerated by the action of dilute potassium iodide solutions," *i. e.*, he considers it intensifies original fog nuclei just as it does exposure nuclei. Although this no doubt takes place (but not by *keimblosslegung*) there is an independent fogging action, as shown by the effect with developers *not* showing development catalysis.

Summary.

1. The Lainer effect, acceleration of development by dil. solutions of iodides, has been investigated, and shown to affect chiefly organic developers of low reduction potential such as hydroquinone.

2. It is shown that the principal effect is to overcome the induction with such organic developers, consequently *increasing* the Watkins factor.

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[1] Similarly to colloidal gold as described by one of us in "Investigations on the Theory of the Photographic Process," p. 208. Longmans, Green and Co., London, 1907.

[2] *Phot. Korr.*, 50, 459 (1913).

3. The effect is ascribed to increased adsorption and complex formation as between silver halide and developer. The bearing of this on the theory of development is discussed.

4. In addition there is a fogging action of dilute potassium iodide solutions on silver bromide emulsions, which is ascribed to nucleus infection of the grain.

Rochester, N. Y.

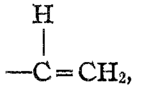
[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

THE ORIENTATION OF MOLECULES IN SURFACES, SURFACE ENERGY, ADSORPTION, AND SURFACE CATALYSIS.

V. THE ADHESIONAL WORK BETWEEN ORGANIC LIQUIDS AND WATER.[1]

By William D. Harkins, George L. Clark and Lathrop E. Roberts.

Received January 12, 1920.

In 1913 Hardy[2] showed that the magnitude of the work done by the attraction between the surfaces of an organic liquid and water during their approach to form an interface, is characteristic for a number of classes or organic liquids. Later Harkins, Brown, and Davies[3] found that whenever the organic liquid contains polar groups in its molecules, this work is very much larger than when they are absent; so much higher that the data made it evident that at the interface such polar groups as —OH, —COOH, —CHO, —CN, —$CONH_2$, —SH, —NH_2, —$NHCH_3$, —NCS, —COR, —COOM, —COOR, —NO_2,  $-\overset{\displaystyle H}{\overset{|}{C}}=CH_2$, —C≡CH, or groups which contain oxygen, nitrogen, sulfur, iodine, bromine, chlorine, double or triple bonds, turn toward the water. The work of Langmuir[4] indicates a similar orientation in monomolecular surface films of organic substances. A theory of heterogeneous equilibrium worked out by Harkins and King[5] indicates, however, that the orienting forces in the case of such *monomolecular* organic films are in general more powerful than those at the surface of the pure organic liquid, and also greater than those acting on the organic molecules at the interface with water. From the standpoint of the theory

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[1] Practically all of the data in this paper were determined during the years 1914–17 or earlier, as the work was interrupted by the war. Some of the data presented here were obtained in this laboratory as early as 1912.

[2] *Proc. Roy. Soc.* (*London*), 88A, 303–33 (1913).

[3] This Journal, 39, 354–64 (1917); also Harkins, Davies and Clark, *ibid.*, 39, 541–96 (1917).

[4] *Met. Chem. Eng.*, 15, 468 (1916); This Journal, 39, 1848–1906 (1917); *Proc. Nat. Acad. Sci.*, 3, 251–7 (1917).

[5] This Journal, 41, 970–92 (1919).