

carded unless the data show this to be a clear cut necessity. Under this general principle, they propose that the following 14 generic names of fishes, in regard to which a difference of opinion exists, shall be provisionally legitimized with the types indicated:

Aëtobatus Blainv., 1816 (type, *Raja narinari* Euphrasen); *Conger* Cuv., 1817 (*Muraena conger* L.); *Coregonus* Linn., 1758 (*Salmo lavaretus* L.); *Eleotris* Bloch & Schneider, 1801 (*gyrinus* Cuv. & Val.); *Epinephelus* Bloch, 1792 (*marginalis* Bloch); *Gymnothorax* Bloch, 1795 (*reticularis* Bloch); *Lam-petra* Gray, 1851 (*Petromyzon fluviatilis* L.); *Malapterurus* Lacépède, 1803 (*Silurus electricus* L.); *Mustelus* Linck, 1790 (*Squalus mustelus* L. [= *Mustelus laevis*]); *Polynemus* Linn., 1758 (*paradisaeus* L.); *Sciaena* Linn., 1758 (*umbra* L. = *Cheilodipterus aquila* Lacép. as restr. by Cuvier, 1815); *Serranus* Cuv. (*Perca cabrilla* L.); *Stolephorus* Lacép., 1803 (*commersonianus* Lacép.); *Teuthis* Linn., 1766 (*javus* L.).

The secretary of the commission will delay the vote on this case until one year from date, in order to give to the profession ample opportunity to express concurrence or dissension as respects any or all of these names.

C. W. STILES,
Secretary to Commission

WASHINGTON, D. C.

SPECIAL ARTICLES

NOTE ON THE THEORY OF PHOTO-GRAPHIC SENSITIVITY¹

THE very small amounts of substance involved in the formation of photographic latent images have prohibited conventional methods of chemical analysis. The ingenious attempt of P. P. Koch² to apply the Ehrenhaft condenser method to the initial reaction of silver bromide in light has apparently not yet given unobjectionable results. But in any case, the use of gelatin-free silver halide can not yet be regarded by the photographic chemist as significant for the gelatin-silver bromide of photographic emulsions. The generally accepted conclusion that the substance of the latent image in these consists of absorbed colloid silver has been reached by indirect methods, and is largely due to Lüppo-Cramer.³

Reasoning from the general principle that the fundamental photographic reaction $\text{Ag}^+ + \theta = \text{Ag}$ is autocatalytic in character, various investigators have suggested that the precursor of the latent image, the

"sensitivity" of the silver halide grains, might itself be substantial in nature, and indeed actually itself colloid silver. Thus R. Abegg⁴ brought forward evidence, inconclusive but suggestive, for "sensitizing" by finely divided silver. The idea that the "ripening" of silver bromide emulsions was associated with a partial reduction forming "Reduktionskeime" was advocated by J. M. Eder,⁵ although this investigator regarded both the "Reduktionskeime" and the latent image as subhalides of variable composition Ag_mBr_m $\text{Ag}_m\text{Br}_{m-n}$. Evidence for the existence of such colloid silver nuclei in relation to sensitivity was brought forward by Lüppo-Cramer,⁶ who found that the sensitivity of "ripened" emulsions could be reduced greatly by treatment with silver solvents such as a mixture of chromic and sulphuric acids prior to exposure. Again, one of the writers and A. P. H. Trivelli⁷ showed that the development of latent images by fuming with ammonia, whereby a recrystallization of silver bromide on silver nuclei was effected, was accompanied by partial reduction of the halide to silver, increasing the probability that such reduction took place in the ammonia ripening of gelatino-silver bromide emulsions. The theory that sensitivity, at least in high speed photographic emulsions, is due to colloid silver was put forward in a very striking form by F. F. Renwick.⁸ He suggested that the change involved on exposure of these is entirely limited to the preexistent colloid silver, which he supposed to be converted by light from a charged "sol" form to a neutral "gel" form, the former being incapable of initiating development, the latter able to act as nuclei for the actual reduction of the silver halide by developers. Quite independently, F. Weigert⁹ brought forward evidence that in "printing out" with silver chloride plus silver citrate, the actual light sensitive substance was colloid silver; that this reacted initially according to the Einstein photochemical equivalence principle, one quantum $h\nu$ being photochemically absorbed per atom of (colloid) silver.

Proof or disproof of this hypothesis is equally difficult to obtain. But inferential evidence of the same character as that regarded as establishing the nature of the latent image has been obtained by the writers recently. In a recent paper¹⁰ they have pointed out that a discrimination between the hypotheses that sensitivity is due (a) to a photocatalyst, *e.g.*, colloid sil-

⁴ *Arch. wiss. Phot.* 1, 18 (1899).

⁵ Cf. Lüppo-Cramer, *op. cit.*

⁶ *Phot. Mittl.*, 1909, p. 328.

⁷ "The Silver Bromide Grain of Photographic Emulsions," 1921, p. 25 (Van Nostrand, N. Y.).

⁸ *J. Soc. Chem. Ind.*, 1920, p. 156T.

⁹ *Sitz. ber. Bul. Akad.*, p. 641 (1922).

¹⁰ *J. Frankl. Inst.*, 1922, p. 486.

¹ Communication No. 185 from the Research Laboratory of the Eastman Kodak Company.

² *Zeit. für Physik*, 3, 169-74 (1920).

³ *Das latente Bild.* (W. Knapp, Halle; 1911).

ver, in the silver halide grains, (b) to the quantum character of light radiation in relation to size of grain,¹¹ might be obtained by Lüppo-Cramer's desensitizing action with chromic acid *et similibus*.

In a subsequent letter to the *British Journal of Photography*¹² it was pointed out that this required that the desensitizer be removed from the emulsion prior to exposure, as otherwise it might act during exposure by destruction of nascent latent image. By methods which will be described in a fuller communication they have shown this to be possible, and extended the desensitizing reaction to layers one-grain thick¹³ for which diffusion phenomena are practically negligible, and which are susceptible of microscopic statistical investigation. With these they have succeeded in showing that the desensitizing effect is a function of grain size, being less for large than for small grains in the same emulsion. This reaction, in itself, does not necessitate Lüppo-Cramer's conclusion that the chromic acid, or other oxidizer, must be acting as a *silver solvent*. It is equally conceivable that some, perhaps reducing, substance derived from the gelatin is acting as the photocatalyst and is destroyed by the chromic acid. Lüppo-Cramer's observation that the desensitizing action becomes more and more effective as the ripening (by digestion) increases is suggestive, but not cogent, evidence for the "silver" hypothesis. He has, however, furnished another method of attack which we have employed. In explanation of the acceleration of development with certain developers by prebathing with potassium iodide,¹⁴ Lüppo-Cramer brought forward the hypothesis of "Keimblosslegung," *i.e.*, the hypothesis that the partial conversion of silver bromide to iodide made occluded colloid silver of the latent image more active. This hypothesis was contested by one of the authors and G. Meyer¹⁵ on certain grounds which need not be recapitulated here. Lüppo-Cramer has pointed out¹⁶ that his hypothesis does not rest on the development acceleration alone, but is more strongly supported by the following observation. If a plate is divested of the soluble non-occluded latent image by chromic acid mixture, it gives practically no image with physical (acid silver) development. If such a plate is now treated with potassium iodide and developed, a full image is obtained. This Lüppo-

Cramer attributes to the "Keimblosslegung" of the occluded latent image. We have repeated these experiments in detail, and with variations to be described more fully elsewhere. Although not convinced that the "Keimblosslegung" is a satisfactory explanation of the development acceleration previously noted, we consider that Lüppo-Cramer's position in regard to the oxidation experiment is well grounded. In particular, the fact that a *repetition* of the sequence chromic acid : potassium iodide yields *no* image strongly supports the view that the first iodide treatment does set free the occluded colloid silver nuclei. Now we have applied this reaction to the *desensitizing process* with chromic acid described above, and find that treatment with potassium iodide after chromic acid gives practically the same effect as treatment with iodide alone; but a further treatment with chromic acid enormously reduces the sensitivity. The similarity of this to the reaction of the *latent image* is evident.

If the desensitizing action of the chromic acid consisted in destroying a reducing substance from the gelatin, there is no apparent reason why this should be reformed by iodide. On the other hand, if the action of such a substance consists in a slight reduction of the silver halide, some part of the reduction product, colloid silver, being occluded in the grain, it is comprehensive that iodizing would again bring it into activity, *i.e.*, to the surface of the grain.

These results are in harmony with the localization of the "sensitivity" in "spots" or "centers" on the grain, as demonstrated by Svedberg¹⁷ and confirmed by Toy.¹⁸ It appears that any quantum theory of exposure must be limited to collisions with sensitive spots, *probably of colloid silver*, and consisting of only a few atoms of metallic silver. A restriction of this character has been recognized as necessary by Silberstein in a modified form of his theory¹⁹ in consequence of measurements of Jones and Schoen²⁰ which showed that in Trivelli and Righter's experiments some 300 quanta of λ 420 μ were incident per grain of 1 μ diameter.

We may suppose that the first action of light is to release a photo-electron from the colloid silver speck. This would require less energy than to release one from the bromide ion of the Ag^+Br^- lattice, owing to the strong electro-affinity here. The colloid metallic silver may be considered as a lattice of silver atoms intermeshed with a lattice of electrons, the latter being active both in conduction and photo-electrically. The free electron, having a kinetic energy $\frac{1}{2}mv^2 = h\nu$,

¹¹ L. Silberstein, *Phil. Mag.*, 44, 257 (1922), A. P. H. Trivelli and L. Righter, *Phil. Mag.*, 44, 252 (1922).

¹² *Brit. J. Phot.*, 1922, p. 51.

¹³ On the technique of these, see Wightman, Trivelli and Sheppard, *J. Phys. Chem.*, 27, 7 (1923).

¹⁴ The so-called Lainer effect; *cf.* Lüppo-Cramer, *Kolloidchemie und Photographie*, 2nd Ed., p. 63 (1922, Steinkopf, Dresden).

¹⁵ *J. Amer. Chem. Soc.*, 42, 689 (1920).

¹⁶ *Koll. Zeitschr.*, 30, 186 (1922).

¹⁷ *Phot. J.*, 62, 186, 310 (1922).

¹⁸ *Phil. Mag.*, 44, 352 (1922).

¹⁹ *Phil. Mag.* (in press).

²⁰ *J. Opt. Soc. Am.*, 7, 213 (1923).

where ν is the wave-length of the active light, is then able to enter the silver ion, forming a neutral silver atom $\text{Ag}^+ + \theta = \text{Ag}$, while the unneutralized bromide ion loses an electron. $\text{Br}^- = \text{Br} + \theta$. This chain reaction, analogous to that suggested by Bodenstein for the action of light on $\text{H}_2 + \text{Cl}_2$, would go on to a limiting state, depending on the initial energy of the photoelectron, but producing a nucleus large enough to initiate development for a developer of given reduction potential.

A fuller account of the experimental work is to be published in collaboration with Mr. A. P. H. Trivelli.

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A METHOD OF ULTRAMICROSCOPY WHEREBY FLUORESCENCE IN THE CYANOPHYCEAE AND DIATOMA- CEAE MAY BE DEMONSTRATED

AT the recent meeting of the Royal Society of Canada I demonstrated the fluorescence of the Cyanophyceae. On returning to my laboratory I succeeded by the same means in finding that nearly all diatoms which I could find are also visibly fluorescent. In this regard the pigments involved stand in contrast to chlorophyll, inasmuch as the latter when in the living cell is not visibly fluorescent save when viewed spectroscopically, or by means of ultraviolet light. Raehlmann¹ believed, however, that he could detect it in suspensions by means of the ultramicroscope, but the fact was called in question by Czapek.² The reason of the non-visibility of the fluorescence of chlorophyll lies in the physical relation of this pigment to its carrier, so that the complex behaves optically like an emulsion or solid solution as, *e.g.*, chlorophyll in paraffin as J. Reinke³ showed. It is, I think, possible to detect, by the optical means to be mentioned, slight evidences of the fluorescence of chlorophyll in the chloroplasts of *Spirogyra* and in some other plants, but they are not convincing. Not so, however, the phycoerythrin of the blue-green algae and a certain red-fluorescent pigment in the diatoms. The following optical conditions enable one to observe this. They furnish indeed the most astonishingly striking and beautiful object pictures of these organisms one can imagine.

The necessary condition to achieve this result is that the organisms be viewed by means of brilliant

reflected light derived from a dark field condenser. This can not be done if the glass slide is of the thickness called for by the current rules of the ultramicroscopy game, since then the light which falls on the object does so from beneath, and if the object be translucent, it passes through it towards the observer. If, however, a thin slide, one, that is, about 0.8 mm. thick or less, is used, one can raise the dark field condenser sufficiently high to cause the light cone to be reflected from the upper surface of the cover glass, provided, however, that a dry objective is used. The light now passes downward, so that the object is illuminated from above, and is seen by reflected light. When blue-green algae are thus viewed, the fluorescence of many kinds becomes readily visible. In some it can be seen only somewhat faintly, because of the numerous bright granules which furnish reflecting surfaces and so produce the effect of an emulsion. If, however, the organisms be mounted in glycerin the extraneous light is obviated, when the cells glow with a fervent light with its characteristic fluorescence color. *Rivularia*, *Cylindrospermum*, some species of *Oscillatoria*, rich blue-green by transmitted light (ordinary microscopy) and brilliantly outlined and accompanied by diffraction images when seen at the apex of the light cone, when seen at the apex of the inverted light cone become deep crimson. By meticulously focussing the condenser and objective at the same time, one obtains combinations of outline object pictures and fluorescence of rare beauty. Other species of *Oscillatoria*, some *Chroococcus* forms, and others have a yellower or golden sheen, while a species of *Nostoc* is bright orange. The cells of *Nostoc commune* obtained by crushing a gelatinous filament from some material (from China) given to me by Professor H. M. Richards about twenty years ago, glow deeply red, while the matrix appears a pale blue, perhaps because of adsorbed phycoerythrin.

The visible fluorescence in the diatoms is confined to certain vacuoles which, by transmitted light, appear a pale greenish yellow, and which take up Sudan III. The pigment may be inferred to be oil soluble, and may be a chlorophyll, with the properties of chlorophyll alpha. It is not readily destroyed by heating, as is phycoerythrin. Because of the numerous sources of reflection, the fluorescence can not be seen, or certainly can be seen only with difficulty, unless the material is mounted in glycerin. When thus viewed, the vacuoles, seen as blood-red, stand out in some species with great clearness. In *Navicula* there are two large vacuoles (as currently described) one on either side of the nucleus with its surrounding cytoplasm. Generally two smaller fluorescent vacuoles occupy the ends of the cell. In *Meridion* when small there may be but one large vacuole. In larger cells three smaller ones may occur. A circular colony of

¹ Raehlmann, E. Neue ultramikroskopische Untersuchungen über Eiweiss, etc. *Arch. ges. Physiologie*, 112: 128. 1906.

² Biochemie der Pflanzen. 1: 564.

³ Die optischen Eigenschaften der grünen Gewebe, etc. *Ber. d. D. B. G.* 1: 395. 1883.