

Recent Contributions of Chemistry to Photography

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ADVANCE in photography in the last two years has not been marked by radical innovations such as new processes, but rather by a deepening of knowledge of fundamental processes and the opening up of new points of view. At the same time the sum of progress in all directions, theoretical and applied, has been considerable. The reviewer has had to condense this article from a preliminary survey of some four times its present magnitude, and even then scant justice was done to the more important subjects. The present review is, therefore, selective; many interesting items must pass unnoticed, and others be only imperfectly documented.

SUPPORT OR BASE FOR SENSITIVE COATINGS

Many new compositions of cellulose, and of its nitrates and acetates, have been patented, as well as new methods of manufacture of the acetates. The number of commercially available solvents appears to be increasing, and in this connection the hydrogenation derivatives of benzene and naphthalene show promise.

GELATIN AND EMULSIFYING MEDIA

During the past two years contributions of physical chemistry to the technology of gelatin and glue have continued. The writer has dealt recently with the role of gelatin in the photographic process,^{1,*} and a brief account must suffice. The function of gelatin in photography has two main aspects: first, in emulsion making; second, as a colloid vehicle of the developable, developing, and developed image. Of the former, the statement of B. V. Storr² on the insufficiency of the physical properties as guides to the suitability of gelatins for emulsions and the relative unimportance of the more obvious chemical properties holds true. In this connection a paper by F. L. Seymour-Jones³ on the "Chemical Constituents of Skin" deserves note as a compact and up-to-date account of the proteins and albuminoids of hide substance.

On the second count, progress has been steady. H. R. Procter's theory of swelling⁴ as a function of chemical combination has been mathematically and experimentally confirmed by J. A. Wilson⁵ and by J. Loeb.⁶ The last named has cogently demonstrated the unique importance of the hydrogen-ion concentration for all primary physical and chemical reactions of the ampholyte, gelatin. Donnan's membrane equilibrium and the determination of pH are likely to assume almost as fundamental importance for photographic processes as for tanning. The depressing action of neutral salts on swelling in presence of alkaline developers is in agreement with this result.⁷

It is likely, however, that some part remains for the suspensoid colloid theory, particularly after treatment of gelatin with dehydrating and tanning agents. The important contributions of R. H. Bogue,⁸ C. R. Smith,⁹ and H. Oakes¹⁰ to the structure theory of gelatin solutions and jellies demand notice in this same connection, as also the development of

more precise methods of measurement of such properties as "jelly strength" (elasticity), "setting point," viscosity, etc.¹¹ Moreover, from the photographic standpoint, the nonisotropic character of the swelling and drying of gelatin jellies is of considerable importance, and the writer and F.

A. Elliott¹² have suggested that this and certain hysteresis factors can be explained without internal structure theories.

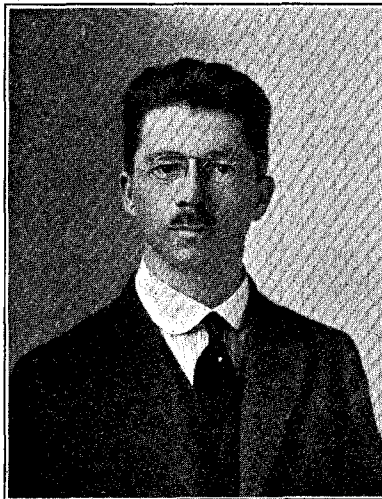
While nothing has yet displaced gelatin as general carrier for sensitive salts, mention may be made of J. Rheinberger's¹³ work on modifications of collodion, and on the Cellophane Company's¹⁴ processes for utilizing viscose cellulose as carrier of silver halides, generally formed by impregnation.

NEGATIVE EMULSIONS, AND THE LATENT IMAGE

With respect to fundamental negative material of photography, the gelatino-silver bromide emulsion, no small progress is to be recorded. It was known that in coarser grained emulsions the grains were crystalline, and investigations in the Research Laboratory of the Eastman Kodak Company¹⁵ have shown that the crystals are entirely of the regular system,

and the diakisdo-decahedral class. This remains true for solid (homogeneous) solutions of bromide and iodide. Wilsey¹⁶ has shown that the effect of the iodide is to change the lattice spacing somewhat, also that the grains of the finest colloid emulsions are crystalline, of the same system. The suggestion of Trivelli and Sheppard¹⁷ that "silver iodide acts as a crystallization buffer substance**** restricting increase in size of grain" was confirmed by C. A. Schleussner and H. Beck¹⁸ in a study of primary gelatino-iodo-bromide emulsions. Precipitation of iodide with bromide lessens the crystallization of the grains. They also note that the optimum iodide content depends upon the emulsification process, and lies between 1 and 5 per cent. An interesting optical sensitizing effect for red light by iodide (and cyanide), discovered by F. F. Renwick,¹⁹ has been shown by Sheppard²⁰ to be specific to certain emulsions. While Renwick attributes it to a direct coagulating effect on silver amierons already present, Sheppard suggests that it is due to an orienting effect of iodide on colloid silver formed by exposure itself. The panchromatic sensitizing by bathing plates in bisulfite followed by alkaline washing, observed by Capstaff and Bullock,²¹ is also attributed to optical sensitizing by colloid silver, in line with Lüppo-Cramer's original discovery.

The distribution of sizes of grain in an emulsion as affecting its photographic properties, attention to which was first directed by Mees, has become the subject of important work. R. Slade and G. I. Higson²² broke ground in this direction, correlating the steep gradation of "photomechanical process" plates with uniformity of grain size. This has been questioned by Renwick,²³ but seems to have a limited validity, provided the sensitivity distribution follows the size. The general question of the relation of sensitivity of grains to



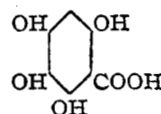
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their size has been brought to the fore by The. Svedberg²⁴ and collaborators. This well-known colloid chemist introduced a very valuable method of grain analysis; preparing a one-grain layer, in a manner similar to that of other workers, after definite exposure steps and development he removed the developed silver grain with a silver solvent. He was thus able to determine by difference counts and size measurements the grains made developable by light (and other agencies, as X-rays, α -rays, hydrogen peroxide) and found not only that grains of the same size might have different sensitivity, but also that within the same emulsion the sensitivity increased with size of grain. The size-classification methods used by Svedberg were comparatively rough. More precise and closer methods have been developed and used by E. P. Wightman and S. E. Sheppard,²⁵ and by Wightman, Trivelli, and Sheppard,²⁶ by which the size-frequency curves of a large number of emulsions of widely differing "speeds," etc., have been measured. These results show again a very general correlation of "speed" with grain size. In their work Svedberg and Anderson found in the case of α -rays that the projective area of a grain determined its chance of being hit, and referred to the possibility that exposure to light might follow a similar law, if light had a discrete nature, as suggested by Einstein and J. J. Thomson. A "normal" law of exposure, based on such a hypothesis, had already been suggested by Ross;²⁷ the hypothesis was mathematically developed by L. Silberstein²⁸ on the assumptions (a) that a grain becomes developable when fully hit by one quantum, and (b) that the chance of being hit is proportional to the projective area of a grain or contiguous clump of grains. Silberstein's formula found close experimental confirmation by A. P. H. Trivelli and F. L. Richter²⁹ using Svedberg's procedure. This result raises the issue, whether the variable "sensitivity" of grains of the same emulsion is purely a question of projective area and quantum encounter, or whether inherent sensitivity differences exist; such differences are feasible on the hypothesis that the grains contain reduction nuclei, e. g., the "Reifungs-Keime" suggested by J. M. Edér, and by the existence of which Lüppo-Cramer³⁰ has interpreted many interesting observations. In fact, in the second Hurter and Driffield Memorial Lecture, F. F. Renwick,³¹ after ably marshaling the strong evidence that the latent image consists of colloid silver dispersed in silver halide, suggested that its formation, at any rate in "high speed" plates, is due, not to photochemical decomposition of silver halide, but solely to a photoelectric coagulation of silver amicros to neutral particles capable of acting as nuclei in development. This view has been criticized,³² but there exists considerable evidence for a primary role of sensitizing nuclei.³³ The issue has been more sharply defined by very recent work of Svedberg.³⁴ He has refined his method of grain analysis by utilizing M. B. Hodgson's³⁵ observation that on early interruption of development of a single grain layer, development is found to have commenced at one or more centers in the grain. Svedberg assumes that these centers are distributed according to the laws of chance, and a grain becomes developable if possessing one or more of a certain size. The probability expression derived for relation to size of grain and chance of developability agreed with observations for two size-classes of grains exposed to light and X-rays. The outcome of work in this direction is of capital importance, not only for the theory of photographic emulsions, but for radiation theory.

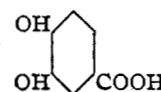
DEVELOPERS AND DEVELOPMENT

The gamut of photographic possibilities is fairly well covered by existing developing agents. Hence the introduction of new ones, if photographically adequate, is likely to depend mainly on production cost. *p*-Amino-carvacrol,

derived from *p*-cymene,³⁶ a by-product of the pulp industry, has not come into use. "Neol" (*p*-amino-salicylic acid) introduced by Hauff & Company with the usual claims of abnormal capabilities,³⁷ has been found³⁸ to belong to the "slow" group, like hydroquinone. A useful review of organic developers has been made by A. and L. Lumière and A. Seyewetz.³⁹ These authors also⁴⁰ find that the reported developing properties of the leuco-bases of rosaniline dyes⁴¹ were probably due to impurities. The question of constitution has been further discussed by B. Homolka,⁴² who concludes that the failure of gallic acid and protocatechuic



Gallic acid



Protocatechuic acid

acid to develop is due to anhydride condensation between the COOH and a para-OH group; if prevented, such substances develop. The possibility of more accurately relating constitution to developing power (as reduction potential) is increased by A. Nietz'⁴³ work on the physical chemistry of development, particularly by his improvement of Sheppard's method of determining reduction potentials by bromide depression of density. The formation of an initial adsorption compound of developer and silver halide is suggested and experimentally supported by Sheppard and Meyer.⁴⁴ Such adsorption effects, including both displacement of one adsorbent by another, and incipient peptization, probably play a large part in the effects observed by Lüppo-Cramer⁴⁵ of dyes in development. These included accelerating, restraining, and fogging effects. A. Steigman⁴⁶ has brought out interesting results, bearing on the difference between physical and chemical development, in his studies in the reduction of silver solutions by sodium hyposulfite.

In relation to manufacture, a process assigned to The Barrett Company⁴⁷ for the catalytic oxidation of benzene to quinone is of interest, and one of F. F. Kitchin⁴⁸ for the electrolytic oxidation of benzene in 10 per cent sulfuric acid to quinone, while the electrolytic manufacture of *p*-amino-phenol⁴⁹ has been described by A. S. MacDaniel and collaborators.

DESENSITIZING AND DESENSITIZERS

Logically this should be discussed in connection with emulsions and the latent image. Practically, Lüppo-Cramer's noteworthy discoveries have joined it up with development. Following up his observations on the desensitizing action of organic developers, notably amidol, he found this due to their oxidation products.⁵⁰ This led him to search for dyes that might, in small quantities, act as desensitizers in development. In phenosafranine⁵¹ he found a desensitizer, such that pre-treatment for 1 min. in a 1:2000 solution allowed an exposed plate to be developed in strong yellow light; by addition to the developer white light could be used.⁵² In many cases, however, the alkalinity of the developer precipitates the free dye base. Besides dyes of the safranine class, Methylene Blue, Auramine O, and Brilliant Green were found effective, but liable to fog. This fogging appears to be general for basic dyes, but may be neutralized by acid dyes, such as Erythrosine, without destroying the desensitizing effect. In a later paper, Lüppo-Cramer⁵³ concludes that this type of desensitizing is an oxidation process, affecting the nascent latent image. The apparent improbability of an oxidation process occurring in the presence of developers of high reduction potential is met by A. Steigman⁵⁴ with the suggestion that the desensitizer is adsorbed strongly compared with the developer.

FIXING AND HARDENING

The physical chemistry of the acid-fixing bath in relation to gelatin has been investigated by Sheppard and collaborators.⁵⁵ The reinforcement of the action of formalin by salts such as sodium sulfate, for hardening prior to development has been patented in England.⁵⁶ In the recovery of silver from waste "hypo" the zinc dust method has been considerably used,⁵⁷ and A. Steigman⁵⁸ has proposed the use of sodium hyposulfite.

INTENSIFICATION AND REDUCTION

Besides the application of various toning processes to intensification, the only noteworthy item is the modification of Lumière and Seyewetz⁵⁹ of the chromium intensification process by the use of salts of chlorochromic acid. These authors also discuss the use of *p*-quinone⁶⁰ in intensification, bleaching, and reduction. The chemistry of persulfate reduction has received considerable attention. The importance of acidity was brought out by Lumière and Seyewetz⁶¹ while S. E. Sheppard (with A. Ballard)⁶² and G. I. Higson⁶³ have shown that silver ions catalyze the decomposition of persulfate in the reaction $S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + O$.

POSITIVE PROCESSES

F. Weigert's work on print-out processes has been noted. The photochemistry of thallos chloride is discussed by C. Renz.⁶⁴ J. M. Eder⁶⁵ has used the light sensitiveness of leuco-bases of dyes in collodion for actinometry. Donisthorpe's dye-impression process, for making color prints on paper or other, gelatin coated base by imbibition from a differentially dyed negative, has been further developed.⁶⁶ A dye printing process of the Badische Company is discussed by Eder.⁶⁷ F. Formstecher⁶⁸ has given a good account of the theory of the print-out process in relation of tone to subdivision, while R. Schwarz and H. Stock⁶⁹ found that the release of bromine from exposed silver bromide approximately paralleled the photographic blackening.

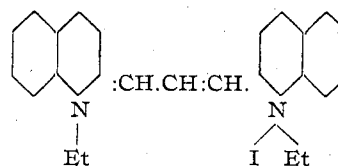
TONING

The most important advance in toning processes is dye mordanting. In this, the silver image is converted either into an insoluble silver compound mordanting dye, as in Traube's diachrome process with silver iodide, or eventually into other insoluble inorganic compounds capable of mordanting. J. M. Blaney⁷⁰ has patented conversion of the image to stannic ferrocyanide; F. E. Ives⁷¹ bleaches the image with potassium ferrocyanide and chromic acid to mordant basic dyes; a copper salt is proposed by J. H. Christensen,⁷² and in a British patent A. Traube⁷³ describes general methods for production of double salts of copper, uranium, iron, etc., to be dyed with basic dyes. The use of iron toned images for mordanting dyes was patented by J. I. Crabtree.⁷⁴

COLOR SENSITIZING

Apart from dye toning, the chief contribution of chemistry to color photography is in dyes for optical sensitizing and selective screening. The impulse given by the war to investigation and production of such dyes in America, Britain, and France has been continued. The isocyanines, resulting from the condensation of quinoline alkylidides or quinaldine alkylidides by alkaline hydroxides, have been investigated very fully by W. J. Pope and W. H. Mills,⁷⁵ although the relations advanced between actual sensitizing power and constitution can only be regarded as provisional. The term carbocyanines has been assigned by these authors⁷⁶ to the important group (of which Pinacyanol = Sensitol

Red is the chief) of dyes produced by the condensation of two molecules of quinaldine alkylidide with one of formaldehyde in presence of alkalies. W. H. Mills and F. M. Hammer⁷⁷ assign to pinacyanol the constitution



This is derived from its mode of formation, its content of two nitrogen atoms but only one acid equivalent, its molecular weight, and products of oxidation. The 3-carbon linkage $:CH:CH:CH:$ is the feature distinguishing carbocyanines from isocyanines. E. O. Adams and H. L. Haller⁷⁸ have described a series of dyes, termed kryptocyanines, obtained from lepidine alkylidides, formaldehyde, and alkali; absorption maximum near $700\mu\mu$, sensitizing at $740\mu\mu$. A general article on the cyanine dyes is due to O. Fischer and Z. Scheibe⁷⁹ while A. and L. Lumière and H. Barbier⁸⁰ have described a new series of sensitizing cyanine dyes. Pantochrome from the condensation of dimethylamino-quinaldine with dimethylaminobenzaldehyde showed a nearly uniform action up to 700—, with a slight minimum in the blue-green. Pinaflavol, a new sensitizer for green, is described by E. König⁸¹ and J. M. Eder⁸² as superior to pina-verdol.

The effects of isomerism and substitution in the isocyanines, on absorption and sensitizing, are dealt with by F. M. Hammer.⁸³ The reviewer, from a comparison of his own former work with later experience, cannot regard the values of sensitizing powers given as definitive, since so much depends on purification and methods of sensitizing. On the latter, the article by F. M. Walters and R. Davis⁸⁴ and the development of so-called "hypersensitizing" by the use of ammonia, alcohol, and water⁸⁵ may be studied. A recent paper by Mills⁸⁶ describes a new cyanine type of the benzothiazole series, resembling isocyanines in having a $:CH$ linkage; also analogs of the carbocyanines.

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