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Evolution of the Concepts of Photographic Sensitivity

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Many interdependent variables are involved in the processes of manufacture, exposure, and processing of silver halide photosensitive materials. Understanding of the conditions and mechanisms for emulsion grain growth, chemical sensitization, spectral sensitization, latent image formation, and development is facilitated by discussion based upon a number of physico-chemical concepts which have evolved from the earliest days of photographic experience. There has been much controversy over the relevance and validity of alternative hypotheses and theories which have been proposed, adopted, and then vigorously defended, some after they have outlived their usefulness. The purpose of this paper is to trace the historical development of basic concepts of photographic sensitivity with emphasis on principles of physics and chemistry and relevance to emulsion technology.

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The Gelatin Silver Bromide Emulsion

The gelatin silver bromide emulsion was developed between 1871 and 1881 by amateur photographers in England who made and coated emulsions for their own use and shared their methods with others by publication in the British Journal of Photography. The first successful emulsions were made by Maddox in 1871.[1] He stirred a solution of silver nitrate into a solution of cadmium bromide and gelatin and coated the mixture without washing. The emulsions were slightly acid and contained an excess of silver nitrate. After exposure, they were physically developed with pyrogallol. The use of potassium bromide and washing by dialysis were introduced by King in 1873.[2] In the same year, Johnston used an excess of cadmium bromide and washed the shredded gel.[3]

The early gelatin silver bromide emulsions had no sensitivity beyond the blue. Vogel discovered in 1873 that collodion silver bromide plates could be sensitized to the green and yellow with the magenta dye, coralline.[4] Eder in 1884 found that erythrosin was an efficient sensitizer of gelatin silver bromide emulsions for the green and yellow.[5,6] Cyanine was used as a red sensitizer until the discovery of the carbocyanines by Homolka in 1905.[7]

Dramatic increases in sensitivity were achieved in 1876, when Wortley made emulsions by running a solution of silver nitrate into a solution of excess ammonium bromide and gelatine at 80°C.[8] After 15 minutes, the emulsion was chilled and the gel shredded and washed. Bennett then found in 1878 that the sensitivity was steadily increased by ripening an emulsion made with excess ammonium bromide for several days at 32°C.[9] Monckhoven showed in 1879 that ripening increased the grain size and that the process was accelerated by ammonia.[10] In 1880 Abney found that the addition of a soluble iodide to the bromide and gelatin solution reduced fog and allowed increased sensitivity to be achieved by prolonging digestion.[11] Eder in 1880 introduced ammoniacal silver nitrate for emulsion making.[12] By this time it had become generally known that, upon heating a remelted washed emulsion to a temperature between 35 and 55°C, the sensitivity of the silver halide grains was increased to a limit determined by the rapid onset of fog. In the emerging photographic industry, this provided the basis for the second ripening or after-ripening process for the production of fast emulsions. Eder reported in 1881 that both the sensitization and the fog were removed by treating gelatin silver bromide plates with solutions of potassium ferricyanide or of chromic acid, containing potassium bromide.[13] He proposed that the increase in sensitivity resulted from the formation of traces of silver by the reducing action of gelatin on silver bromide in the heated medium and that fog arose when the optimum amount of silver was exceeded.

All this work provided the background for the commercial production of sensitive gelatin silver bromide emulsions by high temperature ripening with excess bromide or by the ammoniacal process to increase grain size, followed by digestion of the remelted washed emulsion to further increase sensitivity. After ten years of essentially empirical work, the manufacture of photographic materials was established and gelatine silver bromide dry plates rapidly displaced collodion silver bromide plates. Methods for emulsion making and plate coating were described by Eder in 1886 but the curtain of company confidentiality soon descended.[14,15] Outside the photographic industry, photographic scientists turned their attention to the study of different aspects of sensitivity.

The Subhalide Theory of the Latent Image

The nature of the latent image had been of concern from the time of the earliest work on silver halide emulsions. The blue violet darkening of freshly precipitated

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silver chloride was described by Beccaria in 1757.[16] Scheele in 1777 then showed that treatment with ammonia dissolved the silver chloride leaving a velvet black powder which was dissolved by nitric acid.[17] He concluded that the black substance which results from light action is nothing but reduced silver. Wetzlar in 1828 found that the blueviolet silver chloride, which was produced with release of chlorine by exposure was not changed by treatment with nitric acid.[18] He concluded that the coloration could not be due to metallic silver and called the product silver subchloride. There were then two theories of the action of light on silver chloride, the silver particle theory of Scheele and the subhalide theory of Wetzlar. Bromine was discovered by Balard in 1826 and he observed that greenish yellow silver bromide was blackened by light.

Eder's work on the sensitizing reducing action of digestion with gelatin and the desensitizing action of oxidizing agents first appeared to support the silver particle theory of chemical sensitization and the latent image.[13] He concluded, however, in 1886 that both sensitization by ripening and a latent image exposure resulted in the loss of bromine from the emulsion grains and the formation of silver subbromide, Ag_2Br as a distinct phase and adopted the subhalide theory.[14] This was followed in 1887[19,20] by the more detailed publications of Carey Lea on the subhalides or photohalides of silver. Eder and Carey Lea found that the latent image was at least partially resistant to attack by nitric acid and this was taken to exclude the possibility of silver nuclei. They believed that the subhalide would resist oxidizing agents and initiate more rapid reduction in the developer than the normal halide.

The acceptance of the subhalide theory delayed progress in knowledge of chemical sensitization and latent image formation for many years. The theory was based largely on the studies of the colored silver photochlorides of Carey Lea. Treatment with nitric acid removes surface silver particles but silver chloride has sufficient solubility to allow development to be initiated by subsurface particles which are protected by the silver chloride and not oxidized immediately by nitric acid. There was no physico-chemical evidence for the existence of the subchloride as a definite phase. Because of their lower solubility, silver bromide and silver bromoiodide require longer periods for the initiation of development by subsurface particles of silver.

The Silver Nucleus Theory of the Latent Image

The subhalide theory dominated discussion of the formation and properties of the latent image until 1899 when it was challenged by Abegg[21,22] and Schaum[23,24] who revived the silver nucleus theory. Eder, who had introduced this theory[13] in 1881, continued to defend the subhalide theory.[25–27] At this time, there were two versions of the subhalide or photohalide theory. In that of Eder and Carey Lea, the properties were determined by distributions of Ag_2X molecules or $(Ag_2X)_n$ clusters formed by chemical or photochemical processes. In the adsorption theory of Abegg and Lüppo-Cramer, the photohalides were formed by distributions of particles of colloidal silver adsorbed on and within the silver halide.[28] The validity of this theory was demonstrated by Lüppo-Cramer[29,30] in 1909 and further confirmation was provided by Reinders[31,32] in 1911. Reinders showed that crystals of the photohalides could be produced by crystallization of an ammoniacal solution of silver chloride containing a suspension of particles of colloidal silver. The colloidal silver could be recovered by dissolution of the crystals in ammonia as had been found by Scheele in 1777.

Lüppo-Cramer found that sensitivity and the reactive surface latent image were removed by treatment with a dilute solution of chromic acid.[29] He showed in 1912 that the much more slowly developable latent image which resisted attack by nitric acid and chromic acid was formed within the grains.[33] It became developable after it was exposed by treatment with a dilute solution of potassium iodide which converted surface silver bromide to the bromoiodide. Lüppo-Cramer was the first to appreciate that both a surface and an internal latent image of silver nuclei are formed during exposure and that the internal latent image is protected from oxidizing agents whereas the surface latent image is destroyed.[34,35]

In 1905, Namias provided powerful support for the silver nucleus theory by showing that treatment of a silver bromide plate with an extremely dilute oxygen-free solution of stannous chloride, a powerful reducing agent, conferred the same properties and developability on the plate as a latent image formed by exposure to light.[36] This was confirmed by Perley in 1910.[37] He found that other reducing agents such as sodium arsenite, sodium hypophosphite, and a diluted photographic developer also produced developable silver nuclei. These nuclei were destroyed by treatment with solutions of chromic acid and other oxidizing agents. Following the work of Lüppo-Cramer and Reinders, there was a steady accumulation of evidence supporting silver sensitization and the silver nucleus theory[35] and the concept that the latent image was formed by silver nuclei on the surface or within the crystal was slowly accepted. Investigations during the transition period were reviewed by Bancroft in a series of papers published in the Journal of Physical Chemistry beginning in 1910.[38,39]

The purely hypothetical subhalide theory was finally displaced in 1925 by the X-ray diffraction studies of Koch and Vogler which were taken to prove that there were only two phases in the silver bromide system, silver and silver bromide.[40]

Physical Properties of Silver Bromide Crystals

The physical properties needed for understanding the mechanisms of photographic sensitivity were studied during the period between 1880 and 1940. Arrhenius observed the spectral dependence of photoconductivity in silver halides in 1887. He had submitted his dissertation on electrical conduction in dilute salt solutions to the faculty of the University of Uppsala in 1884 and was discouraged by their lack of interest in his work. This led to his going first to Leipzig and then to the Institute of Ludwig Boltzmann in Graz where he studied electrical conduction in silver chloride and bromide.[41] Winther in Copenhagen discussed the oxidation-reduction aspects of photochemical processes in 1913.[42,43] He concluded that, in a primary process, the absorption of an energy quantum releases an electron with the oxidation of an entity. The electron is then transferred to a second entity with reduction of this entity. This mechanism was applied to the silver bromide system in 1921 by Fajans and von Beckerath[44] and by Sheppard and Trivelli.[45] They proposed that photoelectrons were released from bromide ions by the absorption of light energy. The photoelectrons were believed to diffuse and combine with silver ions to give silver atoms. There was no discussion of the mobility of the remaining bromine atom until 1929 when Kieser introduced the concept of the positive hole.[46] He pointed out that the site would carry a positive charge after the ejection of the electron and that this positive charge could be displaced by the motion of the valency electrons. In this way, a bromine atom equivalent to one created in the interior during exposure could appear at the surface of the crystal allowing bromine molecules to be formed and released.

Studies of the ionic conductivity of silver bromide by Tubandt in 1921 showed that the conductivity was due to the displacement of silver ions with no transport of bromide ions.[47] The concept of a diffusing interstitial defect was introduced by Joffé in 1923[48] and Frenkel analysed the diffusion and drift of interstitial charge carriers and vacant lattice sites in 1926.[49] Frenkel disorder with interstitial silver ions in silver bromide was studied by Jost in 1933[50] and by Koch and Wagner in 1937.[51] In 1946, Frenkel showed that the surface of an ionic crystal would carry a charge with a compensating space charge within the crystal if there were two different surface formation energies for the mobile structural defects of a pair.[52] With silver bromide in a dry system, the surface has a negative charge from Br^- ions with a compensating sub-surface space charge of Ag_o^+ ions, both with unit charges.

The Eggert Theory of Latent Image Formation

Using the available knowledge of the physical properties, a mechanism for latent image formation was proposed by Eggert in 1926.[53] He was concerned with understanding microscopic observations made after interrupted development and photolytic exposures. These showed that development centers and particles of photolytic silver formed at discrete sites of silver halide crystals. He recognized for the first time that latent image formation involved mobile electrons and mobile silver ions and proposed a concentration mechanism according to which photoelectrons combine with silver ions only in the immediate neighborhood of preexisting silver atoms or particles. This was an important new concept which was consistent with the silver nucleus theory of latent image formation but was not fully appreciated at the time. No property was, however, proposed which would favor one silver particle over all the others as a concentration center.

The Sheppard Silver Sulfide Concentration Speck

The ideas of "Ursilber"and the silver nucleus theory were being slowly accepted by 1925 when Sheppard and his coworkers discovered the role of sulfur compounds such as allyl thiourea and sodium thiosulfate in sensitization by digestion and introduced the concept of the silver sulfide concentration speck.[54–58] Sheppard concluded that this speck had no active role in the primary photochemical process and that it functioned by providing a nucleus for the concentration of silver atoms. An equivalent number of bromine molecules was assumed to be liberated at the surface. The general acceptance of the Sheppard theory displaced the silver nucleus theory of chemical sensitization. This acceptance was reinforced when Gurney and Mott in 1938 provided a mechanism for the concentration process.[59] They proposed that the sulfide speck introduced a deeper trap for a conduction electron than any previously available and that an interstitial silver ion was attracted to the negatively charged speck in the resulting Coulomb field to form a silver atom. The latent image was formed by a sequence of these processes. The accumulated evidence supporting this two stage mechanism for latent image formation was reviewed by Berg in 1948.[60] The direct photolysis concentration theory of Sheppard, and Gurney and Mott then appeared to be firmly established.

Silver-Gold Sulfide Sensitization

Major advances were made with the introduction of gold and sulfur sensitization in 1936 by Koslowsky[61,62] of Agfa in Wolfen together with the azaindene stabilizers by Birr[63] which made effective gold sensitization possible. This was first published in postwar intelligence reports and subsequently in the scientific literature. Mechanisms which might account for the effectiveness of gold sensitization have never been introduced in the direct photolysis theories of latent image formation. These theories assume that the sulfide products of chemical sensitization are photochemically inert.

Thermodynamic Aspects of the Photochemistry of Silver Halides

Between 1923 and 1940, there was much concern over the energetics of the processes of photochemical change in silver halide crystals. With silver bromide, it was believed that silver and halogen were liberated by the absorption of light with wavelengths between 400 and 500 nm with energy quanta between 3.1 and 2.48 eV. Fajans first drew attention to the fact that the energy required for the formation of a silver atom and a bromine atom in the gas phase from a silver bromide crystal was much greater than this.[64] This cast doubt upon the feasibility of the direct photolysis mechanism in this range of wavelengths. Calculations were made by Frankenburger,[65] Fajans,[66] Sheppard and Vanselow,[67,68] and Bodenstein.[69,70] Calculations with more recent thermochemical data[71] give a value of 5.2 eV which may be reduced to about 4 eV if atoms adsorbed at separated surface sites are formed. It is evident that this presents a serious problem for the direct photolysis process of the Sheppard-Gurney-Mott concentration theory in the visible intrinsic range of wavelengths.

Reduction Sensitization

The concept of silver sensitization by gelatin and other reducing agents persisted after 1925 and was discussed by Lüppo-Cramer,[35] Chibisov,[72,73] and others. Carroll and Hubbard[74] described sensitization by digestion with sodium sulfite and Carroll patented sensitization with stannous chloride.[75] It was recognized that the sensitivity of fast negative emulsions was decreased by treatment with a dilute solution of chromic acid which did not attack silver sulfide sensitization.

In 1950, twenty-five years after the introduction of the silver sulfide concentration speck by Sheppard, attention was again drawn to silver sensitization by the work of Lowe, Jones and Roberts.[76] They used a low concentration of stannous chloride for reduction sensitization.[36,37,75] As had been found by Eder in 1881,[13] this was removed with a solution of potassium ferricyanide. Sulfide sensitization is not attacked and they were able to establish the independent occurrence of reduction sensitization and the additivity of reduction and sulfide sensitization. This was followed by many papers and patents on sensitization by gelatin digestion, by organic and inorganic reducing agents and by hydrogen.

The Hamilton Nucleation and Growth Theory

Between 1964 and 1970, in another direct photolysis theory, Hamilton abandoned the then accepted role of the sulfide concentration speck and introduced his nucleation and growth theory.[77–81] In the new theory, he did not include any role for the products of sulfur or of reduction sensitization in the primary photochemical process. According to this theory, the absorption of a photon by a crystal of silver bromide creates a photoelectron and a positive hole. In the modified electron transfer theory of Tani, the absorption of a photon by a dye molecule also creates a photoelectron and a positive hole.[82–85] In these theories, with an ideal ionic crystal as the model, silver and halide ions on surface kink sites carry half unit charges. They attract photoelectrons and holes to form silver atoms and halogen atoms leaving the kink sites with half unit charges of opposite sign. The traps are then reset by the attraction in the resulting Coulomb fields of interstitial silver ions and vacant silver ion lattice sites. The atomic species are unstable and dissociate after a certain lifetime. The nucleation and growth process depends on a statistical sequence of successive reversible cycles of formation, dissociation and recombination of atomic species in which both electrons and positive holes are involved. A thermally stable growth nucleus provided by a pair of Ag atoms is formed when a second event occurs within the lifetime of an Ag atom at a particular kink site. This nucleus then increases in size by the combination of a succession of Gurney-Mott processes and regressive processes caused by trapping of positive holes. A number of bromine molecules, equivalent to the silver atoms of the latent image is liberated at the surface. There is no concentration process and the latent image has a distribution of particle sizes, the largest of which are able to initiate development. Tani has accepted the Hamilton direct photolysis theory.[86] These theories do not require the presence of any products of chemical sensitization for the operation of their primary electronic processes.

Experimental Work with a Thin Sheet Crystal Model System

In 1952, even before the introduction of the Hamilton nucleation and growth theory, it had become clear that there were difficulties with the direct photolysis theories. The thermochemical problems raised by Bodenstein[69,70] and others before 1940 had not been resolved and the work of Berg and Burton[60] on competitive interaction between the internal and the surface latent image seemed to require internal disorder in the emulsion grains, a model for which had never been introduced. It appeared that a model system was needed for research on photographic sensitivity which would allow relevant basic properties to be studied both in the absence and in the presence of the gelatin medium.

A new system was provided in 1953 by thin sheet crystals of silver halides, produced by crystallization of molten discs between glass plates with highly polished plane surfaces.[87–89] It was found that crystals of high purity silver bromide had negligible photoconductivity and no photosensitivity in the intrinsic absorption wavelength region beyond 400 nm. This immediately cast doubt on the relevance of the primary photoelectronic process of the direct photolysis theories for exposures in the intrinsic visible region. The crystals were sensitized by the deposition on their surfaces of not more than 10^{14} Ag atoms cm^{-2} from an atomic beam under high vacuum conditions. The atoms which were mobile on the surface combined to give Ag_2 molecules. They also diffused from the surface into the subsurface region. The crystals were fogged by the deposition of not more than 10^{15} Ag atoms cm^{-2}. It seemed that the formation of a developable surface and internal latent image during exposure of the sensitized crystals had to result from the transfer of silver atoms from some Ag_2 molecules to other Ag_2 molecules to give clusters with the same properties as those in the crystals with 10^{15} Ag atoms cm^{-2}. It was recognized that the system provided an accurate model for a reduction sensitized crystal and suggested the operation of a photoaggregation process for the formation of development centers.[90] It was clearly established that a surface development center on a silver bromide crystal could be provided by a cluster of silver atoms. The sensitivity and development centers were immediately oxidized by a dilute chromic acid solution.

The crystals were also sensitized for the formation of a surface and an internal latent image by Ag_2O, and by Ag_2 molecules formed by its thermal decomposition during cooling from the melting point of AgBr.[89] When lightly annealed crystals sensitized in this way were given a longer exposure, the surface image was solarized and the dislocation structure of the subboundaries of the mosaic structure revealed for the first time by almost continuous decoration with particles of photolytic silver. An internal latent image was formed along the dislocations by a shorter exposure. The points of termination of dislocations at the surface were made visible as localized depressions by treatment with suitable silver halide solvents and sulfide sensitization occurred preferentially at these sites. This work introduced the concept of the dislocation to the theory of photographic sensitivity[91–94] and established that dislocations could play an important role in the nucleation of chemical and photochemical processes.

In the presence of gelatin, the crystals were sensitized by all the methods which are effective with silver halide photographic emulsion microcrystals.[87–89] These included reduction sensitization in which Ag_2 molecules are formed by the reduction of Ag_2O molecules, sulfide sensitization in which adsorbed Ag_2S molecules are formed, and silver-gold sulfide sensitization with sodium aurous dithiosulfate giving adsorbed Ag_2S and (Ag,Au)S molecules. In these methods of chemical sensitization in which nonhalide silver molecules are formed, bromide ions are released at the surface of the silver bromide crystals. The latent image is *initially* produced by the photoaggregation of Ag and Au atoms chemically equivalent to these nonhalide molecules and there is no release of bromine molecules at the surface.

Donor and Acceptor Centers in Photographic Sensitivity

Before crystals of silver chloride and silver bromide of the highest achievable purity show photoconductivity or photosensitivity to wavelengths longer than 400 nm, they have to be sensitized with molecules such as Ag_2, Ag_2O, Ag_2S, or (Ag,Au)S which are photodissociated when adsorbed on silver halide crystals by the absorption of smaller energy quanta than are required for the silver halide itself.[95–97] These sensitizing molecules are adsorbed or incorporated in the grains of most high speed negative commercial emulsions. Surface sensitization is destroyed by treatment with oxidizing solutions and surface and internal sensitization by treatment with an aqueous solution of the halogen.

It is convenient to refer to these sensitizing molecules as donor centers. They introduce bands of occupied electronic energy levels in the energy gap from which electrons can be transferred to the conduction band by the direct absorption of energy quanta. Electron transfer can also result from the local annihilation by Auger processes[98] of excitons of intrinsic polarization waves. With both processes, a positively charged molecule results which rapidly dissociates with transfer of an Ag^+ or Au^+ ion to an interstitial position. In the primary electronic process at room temperature, a photoelectron and an interstitial ion are thus made available for latent image formation and positive holes and halogen molecules are not involved. The role of donor centers in the photoaggregation process was emphasized in 1985.[95,96] Recognition of the concept that both dislocations and donor centers are required in silver halide crystals for a high level of sensitivity with chemical development was important for progress in emulsion technology.[94,97]

Polyvalent cations in lower valency states such as Cu^+, Fe^{2+} and Ir^{2+} may also introduce donor centers and give photoelectrons and interstitial silver ions on exposure. Polyvalent cations in higher valency states such as Cu^{2+}, Fe^{3+}, and Ir^{3+} with lower unoccupied levels in the energy gap may introduce electron acceptor levels from which holes may be transferred to the valence band by the direct absorption of energy quanta or the annihilation of excitons of polarization waves. In this case a charge-compensating vacant silver ion lattice site is eliminated by combination with an interstitial silver ion.[99–101]

In the absence of polyvalent cations, there are initially no deep acceptor centers in the grains of chemically sensitized silver halide emulsions. Acceptor levels with lower unoccupied electron states are first introduced as Ag_4^+, and $AuAg_3^+$ latent image growth nuclei and Ag_5^+, $AuAg_4^+$ and larger development centers during exposure. Photoholes may be created at these centers by the direct absorption of energy quanta or the annihilation of excitons of polarization waves. The positive charge is then restored by the adsorption of an interstitial silver ion.[96]

The donor centers provide traps for positive holes releasing interstitial silver ions in the process. This property of Ag_2 and Ag_2S molecules was discussed in 1957. The latent image acceptor centers provide traps for photoelectrons with restoration of the positive charge by the adsorption of interstitial silver ions.[102]

The Silver Halide Emulsion Grain

For many years, fast negative silver halide emulsions were made by the single jet method in which a stream of silver nitrate or of ammoniacal silver nitrate was run, with vigorous stirring, into a solution of alkali or ammonium bromide and iodide and gelatin. This produced grains with a broad size-frequency distribution and cores with an enhanced iodide concentration. It was realized in 1957 that dislocations would be introduced at the inevitable iodide ion concentration gradients.[102,103] Internal latent image formation with surface desensitization would result and this emphasized the need for a homogeneous iodide ion distribution within a silver bromoiodide phase. This was achieved by using a high speed external mixer to produce an ultra-fine dispersion of silver iodide or silver bromoiodide or by the use of an iodide ion releasing compound.[104–108]

It was also appreciated that the efficiency of spectral sensitization would be increased by increasing the surface-to-volume ratio of the grains. This led to the production of thin tabular grains by double or multiple jet methods in which solutions of alkali halides and silver nitrate were run with vigorous stirring into a solution of gelatin at a pAg of 9.5 to 10.5.[109] Methods were then described for making monodisperse emulsions with thin homogeneous hexagonal tabular microcrystals.[110,111] Controlled densities of dislocations were introduced by the creation of steep iodide ion concentration gradients between two phases.[112] Thin tabular grains with a core-shell structure and a controlled density of edge-terminating dislocations were introduced.[93,94,112] In favorable circumstances, products of chemical sensitization and the surface latent image are formed and chemical development is initiated at these sites with higher probability than at other surface sites.[94]

An optimum density and distribution of donor centers has to be introduced in emulsion microcrystals during growth and chemical sensitization. The formation of Ag_2 molecules along dislocation lines has to be minimized as these would provide growth nucleus precursors for internal image centers which would compete with and desensitize the surface. The critical problem with dislocations in emulsion technology for a high-performance surface-imaging- system is to suppress internal image formation along dislocation lines while enhancing surface latent image formation at their sites of termination.[101]

Spectral Sensitization

The Sensitizing Dyes. After having resolved the thermodynamic problems of latent image formation in the visible intrinsic range of wavelengths by the introduction of sensitizing donor and acceptor centers, we can now return to the evolution of the concepts of spectral sensitization which also requires the presence of these centers. We left this subject at the beginning of the century when erythrosin and cyanine were still used for panchromatic sensitization. The era of cyanine dye sensitization began in 1902 when Miethe and Traube of Berlin patented the use of an isocyanine, ethyl red.[113] This dye gave stronger orthochromatic sensitization from the blue green to orange than erythrosin. A more efficient red sensitizer, pinacyanol, was synthesized by Homolka and patented in 1905.[7] The structures of these and other cyanine dyes which were marketed by the German dye industry were established by Pope and Mills and their coworkers[114,115] at the University of Cambridge between 1916 and 1920. Cyanine which was synthesized from 4-methylquinoline amyliodide in alkaline oxidizing conditions, was shown to be 1,1'-diamyl-4,4'-cyanine iodide. Ethyl red was found to be 1,1'-diethyl-2,4'-cyanine iodide. It was synthesized from 2-methyl quinoline ethiodide and quinoline ethiodide. The third cyanine isomer, 1,1'-diethyl-2,2'-cyanine iodide was synthesized in 1920 by Fischer and Scheibe[116] from 2-methylquinoline ethiodide and 2-iodoquinoline ethiodide. It was also an orthochromatic sensitizer.

In pinacyanol, two quinoline nuclei are joined by a trimethine chain giving the structure, 1,1' -diethyl-2,2'-carbocyanine iodide.[117,118] This dye was synthesized from 2-methyl quinoline ethiodide and formaldehyde or ethyl orthoformate. Most of the photographic sensitizing dyes produced between 1902 and 1920 were cyanines or carbocyanines with two quinoline nuclei linked by a methine group or by a trimethine chain. Dyes with benzothiazole nuclei were described by Hoffmann in 1887 but they had not been used as spectral sensitizers. Mills repeated this work and determined the structures of the two dyes which were produced, a yellow 3,3'-diethyl-2,2'- thiacyanine iodide and a purple 3,3'-diethyl-2,2'- thiacarbocyanine iodide which was an improved orthochromatic sensitizer.[119] König and Meier in 1925 then used quaternary benzoxazole and benzothiazole alkiodides to synthesize oxacarbocyanines and thiacarbocyanines using the ethyl orthoformate method.[120] This was followed by intensive synthetic activity during which many heterocyclic nuclei including benzobenzothiazole and benzimidazole were introduced. Sensitization was extended to the infrared by increasing the length of the methine chain in penta- and heptamethine cyanines.[121,122] The cyanine and carbocyanine dyes have planar molecules. It was found that many of these dyes formed stable aggregates in solution and in the adsorbed state on silver halide crystals. These aggregates gave intense narrow absorption bands which could be used in multilayer color photographic materials for color separation.

Direct Photolysis Theories of Spectral Sensitization. The electron transfer mechanism for spectral sensitization was first proposed by Gurney and Mott in 1938.[59] They placed the lowest unoccupied level of the sensitizing dye molecule above the bottom of the conduction band so that a photo-excited electron would be rapidly transferred from the dye to the conduction band leaving a semi-oxidized dye free radical. The fate of the radical was not discussed but its relative positive charge would lower the energy levels and promote recombination with the photoelectron. Tani and his coauthors then introduced the modified electron transfer mechanism in 1968.[82–86] According to this mechanism, an electron is transferred from the full band to the lower vacant level of the radical. This process which requires thermal activation generates a mobile positive hole in the full band and returns the dye molecule to its ground state. An electron-hole pair is thus created by the absorption of a photon by the dye molecule. With these mechanisms, the two electronic charge carriers participate in the processes of latent image formation and, for a high quantum efficiency, recombination has to be prevented.

The direct photolysis theories are inconsistent with the well-established insensitivity of crystals of silver halides of the highest achievable purity whether dye sensitized or not.[71,96] Chemical sensitization is essential for sensitivity and there is no evidence for the initial creation and displacement of holes in efficiently chemically and spectrally sensitized crystals. Bromine or other halogen molecules are not liberated at the surfaces of chemically sensitized crystals during the early stages of surface latent image forming exposures and these stages are not sensitized by non-reducing adsorbed halogen acceptor molecules.

Spectral Sensitization and Donor and Acceptor Centers. When the thermochemical problems of the direct photolysis theories for intrinsic and spectrally sensitized latent image formation had not been resolved by 1957, it became clear that new concepts were required. Mitchell proposed a process for spectral sensitization which involved chemical sensitizing molecules with smaller photodissociation energies than the silver halides and with occupied electronic levels in the energy gap.[123,124] In this two-electron process, an electron is transferred from the higher occupied donor level of the sensitizing molecule to the lower unoccupied level of the excited dye molecule giving a semireduced dye free radical with an effective negative charge which raises the occupied levels of the free radical. The electron from the upper level is then transferred to the conduction band. At the same time, a silver ion from the resulting positively charged sensitizing molecule is transferred to an interstitial position preventing recombination. Positive holes are not involved in this primary process and the thermochemical problems are resolved. The process was discussed by Tamura and Hada[125] as the "elevator mechanism" in l967 and by Dorr[126,127] as the "Fahrstuhl" mechanism in 1968. It was extended to cover all sensitizing donor and acceptor centers in 1985 and became an essential feature of the mechanisms for spectral sensitization and desensitization of the photoaggregation theory.[71,128] In 1990, the three interacting electronic charge carrier process was described as an Auger process.[98] With a donor center, the three carriers are provided by the electron in the higher occupied level of the donor center, the hole in the lower level of the excited dye molecule, and the electron in the excited level of the dye molecule. In one continuous process, the energy released by the combination of the donor electron with the hole is transferred to the excited electron which, with an efficient sensitizing dye, passes into the conduction band. The dye returns to its ground state. A corresponding mechanism applies for an acceptor center.[71,128]

Spectral Sensitization and Desensitization. The sensitizing efficiency of a dye decreases as the surface coverage increases and this seriously limits the effectiveness of spectral sensitization. The understanding of this problem required quantitative theoretical discussion with new experimental information.

The polarographic measurements of Stanienda,[129] Tamura and Hada,[125] and the systematic measurements of Large[130] and Lenhard[131] allowed the sensitizing and desensitizing dyes to be arranged in a continually increasing sequence of cathodic halfwave potentials, E_R from the negative potentials of sensitizing dyes such as the benzimidazolocarbocyanines to the positive potentials of desensitizing dyes.[71] This introduced a physical variable which could be used for quantitative analysis. Gilman then made a systematic study of the sensitizing action of the dyes of this sequence[132] and found that, under the conditions of his experimental work, there was a discontinuous change from sensitization to desensitization between – 0.86 and – 0.81 V. There was continuity in the cathodic halfwave potentials but a discontinuity in the sensitizing behavior. The integration of this important observation into the theory of photographic sensitivity presented problems because the polarographic measurements were made at the interface between an electrode and a liquid medium and sensitization and desensitization involved electronic processes at the interface between the silver halide crystal and the dry gelatin medium. These electronic processes had to be introduced and related to the critical property of the sensitizing dye which was measured by the cathodic halfwave potential.

A relation emerged from the study of electron trapping processes in solid state systems which was undertaken by Mitchell in 1983.[133,134] With the methods of statistical mechanics, he treated the photographic emulsion as a canonical ensemble of a very large number of independent systems provided by identical emulsion grains subjected to the same photon flux. The calculations were made for a model with grains of volume $V = 4\mu m^3$ and a number of photoelectrons, distributed between the conduction band and N_t shallow trapping states of depth E_t eV, introduced by adsorbed dye molecules. The linear increase of $\log_{10}(P_t / P_c)$ with $\log_{10}(N_t)$ which was found is given by

$$\log_{10}(P_t / P_c) = \log_{10}(N_t) + 16.89\, E_t - 7.24$$

where P_t is the probability that the electron will be in a trapping state and P_c the probability that it will be in a state of the conduction band.[128,133,134] The calculations showed that $(P_t / P_c) = 1$ for $N_t = 10^4$ and $E_t = 0.19$ eV. The ratio of the probabilities was increased for larger N_t and E_t values corresponding to desensitization and decreased at constant N_t for smaller, including negative E_t values, corresponding to increased sensitization.[71,95,128]

This allowed the physical property of electron trap depth to be related to the polarographic cathodic halfwave potential. The condition, $(P_t / P_c) = 1$ for $N_t = 10^4$ and $E_t = 0.19$ eV, corresponds to a crossover potential of –0.81V from the sensitization studies. From the statistical analysis, $(P_t / P_c) = 1$ for $N_t = 10^6$ and $E_t = 0.07$ eV. A critical study of the available information suggested that this would correspond to a crossover potential E_R of –1.15 V.[134] This allowed the useful empirical relation $E_t = 0.35eE_R + 0.47$ between the electron trap depth of a dye and the cathodic half wave potential to be proposed. From this work, dyes which sensitize under normal atmospheric conditions have E_R values between –1.80 and –1.0 V, and E_t values between –0.16 and + 0.12 eV. Dyes that desensitize have more positive E_R and E_t values.

The statistical studies proved that the dye coverage at the crossover point between sensitization and desensitization increased as the E_R or E_t value for the sensitizing dye became more negative and this accounted for the sensitizing efficiency of dyes with benzimidazole nuclei.[71]

Supersensitization. The superadditivity of spectral sensitization by a mixture of two dyes was discovered by Bloch and Renwick in 1920.[135,136] They found a remarkable increase in sensitivity when pinacyanol (1,1'-diethyl-2,2'-carbocyanine) and what was probably 1,1'-diethyl-6,6'-dimethyl-2,2'-carbocyanine were used[137] together with auramine (4,4'-(imidocarbonyl)bis (dimethylaminophenyl) hydrochloride). Mees introduced the term supersensitization in 1937 and patented a number of supersensitizing combinations including pinacyanol and dialkylaminostyryl dyes.[138] Following this many supersensitizing combinations of dyes were claimed in the patent literature.[71,139] The subject was reviewed by Gilman in 1974.[137] By then it was recognized that the efficiency of spectral sensitization decreased with increasing dye coverage and that J-aggregated dyes often had a low sensitizing efficiency. Many dyes in the J-aggregated state had a high luminescence efficiency and this led West and Carroll[140] to propose that the supersensitizers trapped the excitation from the aggregate and transferred the energy to produce photochemical change in the crystal. At this time, it was believed that a photoexcited dye molecule transferred an electron to the conduction band of the silver halide crystal leaving a semioxidized dye free radical which could release a positive hole or provide a trapping site for an electron. This would result in recombination. After critically analyzing the available information, Gilman proposed his hole-trapping theory[137] according to which supersensitization of J-aggregates resulted from hole trapping giving a semioxidized supersensitizer molecule. This did not resolve the problem that the resulting free radical could recombine with the photoelectron.

It now appears that supersensitization results from the operation of an Auger mechanism at the supersensitizing dye, the same as that which operates at a sensitizing dye.[71,98,139] The sensitizing efficiency decreases with increasing dye coverage for statistical reasons and also as a result of the formation of J-aggregates. The excited J-aggregates tend to decay by fluorescent emission resulting in a low photochemical efficiency. The supersensitizing molecule traps the excitation and, when it is within electron transfer range, accepts an electron from a donor center and transfers an electron to the conduction band by an efficient Auger process. The efficient supersensitizers have E_R and E_t values more negative than those of the dyes which they supersensitize. Examples are provided by benzimidazolo-carbocyanines, cyanines, merocyanines, and styryl dyes as supersentitizers for cyanine, carbocyanine and oxa- and thia-carbocyanine dyes.[71,128,139] The sensitizing efficiency of J-aggregates of dyes with large negative E_R and E_t values such as 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethyl-benzimidazolo-carbocyanine is not significantly increased by supersensitization.[141]

The theoretical work on the statistics of electron trapping processes has been of particular value in contributing to the understanding and definition of the concepts associated with the interaction of donor and acceptor centers and sensitizing and supersensitizing dye molecules.[142]

The Photoaggregation Theory

We now turn to discussion of the formation of latent image growth nuclei and development centers during exposure. The essential underlying concept that development centers are produced by a small number of effective photochemical events was introduced by Silberstein in the 1920s in his quantum theory of photographic exposure.[143–145] According to Silberstein, the formation of development centers and the shape of the characteristic curve are determined by events in which two photographically effective quanta are absorbed. Depending on the sensitivity of the emulsion grain, a number of quanta are ineffectively absorbed before two quanta are effectively absorbed. This results in the displacement of the characteristic curve for a two-quantum process away from the origin along the log E axis. Throughout his publications, this concept was defended by Silberstein who was convinced of its validity, but it was never accepted.[146–149] It has been revived in papers by Ames,[150] Shaw,[151] and Kawasaki, Fujiwara, and Hada.[152] There is experimental evidence for the broad general conclusion that the characteristic curve may have a shape close to that predicted by Silberstein.[153,154] However, the direct photolysis theories of Hamilton and Tani provide no mechanism for a two-quantum process for the formation of a development center.

No convincing analysis of the reasons for the effectiveness of gold and sulfur sensitization, discovered by Koslowsky in 1936, has ever been included in the direct photolysis theories which assume that the sulfide products of chemical sensitization have a passive role during the primary electronic and ionic processes of latent image formation.[100] Experimental observations show, however, that Au atoms are incorporated in latent image centers during exposure.[155–157]

New concepts have to be introduced to allow the integration of the contributions of Silberstein, Koslowsky, and others into the theory of photographic sensitivity. These depend on the role of chemically produced Ag_2 molecules as latent image growth nucleus precursors,[90] and on the role of Ag_2, Ag_2S and (Ag,Au)S molecules as donor centers.[95,96] According to the photoaggregation theory,[158] the latent image is initially formed by the photoaggregation of Ag and Au atoms chemically equivalent to donor centers. Covalent Ag_2S and (Ag,Au)S molecules form strongly adsorbed monolayer islands on the surfaces of silver halide microcrystals. Ag_2 molecules are formed and adsorbed at shallow positive potential wells around the edges of these islands and at other surface sites by the reduction of Ag_2O molecules.[96] These sensitizing donor centers are dissociated during exposure by the annihilation of energy quanta with the creation of photoelectrons, Ag_o^+ or Au_o^+ interstitial ions, and AgS centers.

Isolated Ag and Au atoms are formed by the combination of a photoelectron with an interstitial ion at a shallow positive potential well. These are ineffective loss processes because there is a large number of shallow traps and the probability for the occurrence of a second event at the same site with few events and random walk diffusion of the electrons is very small. These events provide the ineffective processes of the Silberstein theory.

A development center is formed by two effective events.[158] In the first event, a latent image growth nucleus is produced as an Ag_4^+ or $AuAg_3^+$ center by the combination of an Ag_2 molecule, acting as a latent image growth nucleus precursor, with a photoelectron and an Ag_o^+ or Au_o^+ interstitial ion, followed by the adsorption of an Ag_o^+ ion.[159] The positively charged center introduces a site-directing Coulomb field and a deep trap for a subsequently liberated photoelectron. This desensitizes remaining Ag_2 molecules.[160]

For the second effective event, a photoelectron is attracted to and trapped by the latent image growth nucleus and the positive charge is restored by the adsorption of an Ag_o^+ ion giving an Ag_5^+ or $AuAg_4^+$ development center of minimum size. This center grows by the repetition of these processes. The photoaggregation theory provides efficient mechanisms for the two effective events of the Silberstein theory and for latent image formation in silver-gold sulfide sensitized systems.

Chemical Development

Two problems have to be resolved by any acceptable theory of chemical development: (1) how does the liberation of photoelectrons at randomly distributed sites by the absorption of energy quanta result in the formation of clusters of Ag and Au atoms for development centers at only a few sites when the electrons initially diffuse by a random walk process and there are many equivalent sites for the separation of the atoms; and (2) how does a chemical developer differentiate between unexposed and exposed chemically sensitized grains after absorption of a minimum of two energy quanta by a grain?

The first problem is resolved by the basic concept of the photoaggregation theory,[158] namely, the formation at an Ag_2 latent image growth nucleus precursor by two successive effective events during the initial stage of exposure, first of an Ag_4^+ or $AuAg_3^+$ latent image growth nucleus and acceptor or concentration center, and then by the addition of one Ag atom, through trapping an electron and adsorbing an Ag_o^+ ion, of an Ag_5^+ or $AuAg_4^+$ development center of minimum size. These positively charged clusters introduce site-directing centers which attract and trap a photoelectron with restoration of the positive charge by the adsorption of an Ag_o^+ interstitial ion. This gives an efficient latent image growth and concentration process.

The second problem is concerned with the initiation of chemical development. Ag^+ *ions* with a fractional positive charge at surface sites, Ag^+ ions with a unit charge in the aqueous medium, Ag_o^+ interstitial silver ions with a unit positive charge, and small uncharged clusters of Ag and Au atoms cannot accept electrons from reducing molecules in a nonfogging photographic developer.[161] Before electron transfer is possible in the aqueous medium, a small cluster of Ag or of Ag and Au atoms must carry a positive charge. Because the ΔH decrease on transfer of an Ag^+ ion to the aqueous medium is 4.96 eV, an Ag^+ ion must have a binding energy to a cluster that is greater than this. Ag_5^+ is the smallest cluster that, with a binding energy in vacuum of 5.24 eV and additional polarization energy can have a significant lifetime in the aqueous medium. It provides a development center of minimum size. The development center accepts an electron from a reducing molecule and a halide ion passes into solution from near its interface with the grain. The positive charge is restored by the adsorption of an Ag^+ ion at this interface. An $AuAg_4^+$ center with a binding energy of 5.71 eV and a polarization energy of 0.2 eV has a lifetime of 3×10^4 sec and provides a more effective development center.[158,162–164] The increased stability in the positively charged state in an aqueous medium of $AuAg_4^+$ and larger development centers containing Au atoms compared with Ag_5^+ and larger centers with only Ag atoms explains why the incorporation of Au atoms in development centers during exposure is of critical importance.[165] Chemical development is more efficiently initiated when the development centers are formed at sites of termination of edge dislocations.[92–94] With increased exposure, the growth of a development center beyond the minimum size reduces the induction period for the initiation of rapid development,[171] and more development centers may be formed on a grain.

These mechanisms resolve the problem of how the developer differentiates between exposed and unexposed grains. Positively charged Ag_5^+, $AuAg_4^+$ and larger clusters of Ag and Au atoms, produced during chemical sensitization, are fog centers. Unfogged grains have no such positively charged clusters that can initiate chemical development. These clusters are produced during exposure.

The Concentration Process in Latent Image Formation

Studies of exposed optimally sensitized emulsion grains with the optical microscope soon after the initiation of development show that few development centers are formed.[124,166,167] A concentration process must evidently operate in the formation of the latent image. The essential features of the Sheppard concentration process were introduced in 1925 in a paper by Sheppard, Trivelli, and Loveland.[56] According to Sheppard, Ag atoms are concentrated at a few discrete specks of silver sulfide which have otherwise a passive role during exposure. As knowledge of the physical properties of the system increased, it became difficult to understand how this process could operate efficiently in the presence of many equivalent sulfide specks. Sheppard himself observed that the amount of sulfur sensitizer required for maximum sensitivity would give monolayer coverage of the surface of the microcrystals.[168]

A photoelectron diffuses away from its site of creation by a random walk process. At the end of its lifetime, it combines with an Ag_o^+ ion to give an Ag atom which has a lifetime of about 1 sec before dissociation.[163] At the beginning of exposure, there is a very large number of equivalent shallow trapping sites on the surface of a silver halide emulsion grain at which this process can occur. These include surface Ag$^+$ *ions* with a small fractional positive charge and sites associated with adsorbed sulfide monolayer islands. With random walk diffusion, there is a small probability that an Ag atom will be formed at any particular one of these sites. It must be formed at one such site but there is a very small probability for the occurrence of a second event at this site.[133,134]

If a development center is to be formed by the absorption of less than four effective quanta by a silver halide grain, as appears to be the case with the grains of maximum sensitivity in modern high speed negative emulsions, an efficient photochemical process must favor the occurrence of successive events at the same site. This site cannot be created during chemical sensitization as in the Sheppard-Gurney-Mott concentration theory. If one such site were produced, a large number of equivalent sites would be inevitably produced and there could be no concentration process. That the concentration center has to be created by the *first effective* photochemical event is a fundamental concept.[163] The center must introduce a site-directing mechanism so that it efficiently attracts and traps a subsequently liberated photoelectron to reduce the probability for the formation of another concentration center. This property must be restored rapidly after each event.

The free energy of a conduction electron has a large entropy term so that the electron can be localized only by a process which reduces the internal energy term. The first effective electron trapping event must therefore create a positively charged entity at the site. A subsequently liberated photoelectron can then be attracted and trapped with the necessary reduction in the free energy. The positive charge must be rapidly restored after this event.[90,133,134]

At room temperature, an Ag$_2^+$ center has a lifetime of 8×10^{-10} sec and an Ag$_2$ molecule cannot adsorb an Ag$^+$ ion to give a stable Ag$_3^+$ cluster. These centers can therefore not provide an effective site-directing Coulomb field for a photoelectron.[158,162] By one photochemical event, a chemically produced Ag$_2$ sensitization center and latent image growth nucleus precursor is transformed into an Ag$_4^+$ latent image growth nucleus which has a lifetime greater than 10^5 sec in a dry dielectric medium at room temperature.[158] This first effective event creates a site-directing Coulomb field. In a second effective event, this growth nucleus gives an Ag$_5^+$ development center which grows by a succession of electronic and ionic processes in which a photoelectron is attracted and trapped followed by the adsorption of an Ag$_o^+$ ion which restores the trapping state. This provides an efficient concentration process for the growth of the development center.

The concept that a cluster of Ag or of Ag and Au atoms acquires a positive charge by adsorbing an Ag$^+$ ion when it exceeds a small critical size was introduced in 1954.[169] Calculations of the binding energy of an Ag$^+$ ion to small clusters of Ag and Au atoms published in 1978 demonstrated its feasibility.[134,162–165] In the presentation of his nucleation and growth theory, Hamilton has rejected this concept for a concentration process,[78,80,81] and indeed any concentration process. This rejection has been critically discussed in a recent paper.[170]

Quantitative aspects of the concentration process with a positively charged latent image center were first studied in 1981.[95,133,134,170,171] For an AgBr crystal, the mean drift range of a photoelectron in the Coulomb field of a unit positive charge was found to be $r = 32(\mu_D\tau)^{1/3}$ µm with μ_D, the drift velocity, in cm^2 V^{-1}sec^{-1} and τ in sec. At room temperature, r = 0.27 to 0.76 µm. This determines the maximum diameter 2r of a thin tabular grain with a central concentration speck in which an efficient concentration process can operate.[95] A regular thin tabular grain with an edge concentration speck has a smaller optimum diameter.[171]

The mean drift range is proportional to $n_i^{-2/3}$ where n_i is the concentration of Ag$_o^+$ ions. This important variable can be utilized to increase the drift range. The concentration of Ag$_o^+$ ions is reduced by the incorporation of divalent cations such as Cd^{2+} or Pb^{2+} ions or by the adsorption of azaindene stabilizers and heterocyclic mercapto compounds. These additives stabilize the Ag$_2$ sensitization centers and increase the sensitivity of silver halide emulsion grains.[95,171]

Summary and Discussion

At the present time there are two theories of photographic sensitivity, each with its own set of concepts.[96] In its currently accepted form, the direct photolysis theory is represented by the Hamilton nucleation and growth theory of latent image formation[81] with the Tani modified electron transfer theory of spectral sensitization.[86] The alternative approach which is summarized here is provided by the Mitchell photoaggregation theory.[158]

In the photoaggregation theory, the silver halide crystal has partial covalent bonding with fractional charges on *ions* at surface sites.[161] During chemical sensitization, covalent silver sulfide and silver-gold sulfide molecules are formed and strongly adsorbed as small monolayer islands at surface singularities and particularly at the sites of termination of dislocations.[92,94] Silver molecules are formed and adsorbed around the edges of these islands. These Ag$_2$ sensitization centers and sulfide molecules have essential roles in the initial stages of the formation of latent image growth nuclei.[90] They introduce donor centers which are photodissociated by the absorption of smaller energy quanta than are required for the dissociation of the silver halide. Their photodissociation creates photoelectrons and Ag$_o^+$ and Au$_o^+$ interstitial ions, and the Ag$_2$ molecules provide latent image growth nucleus precursors.

Isolated Ag and Au atoms are formed by the combination of a photoelectron with an interstitial ion at one of a large number of equivalent surface and internal shallow positive potential wells.[163] These are ineffective loss processes because there is a large number of shallow traps and a small probability for the occurrence of a second event at the same site with few events and random walk diffusion of the electron.

A development center is formed by two effective events. In the first event, a latent image growth nucleus is formed as an Ag$_4^+$ or AuAg$_3^+$ center by the combination of an Ag$_2$ sensitization center, acting as a latent image growth nucleus precursor, with a photoelectron and an Ag$_o^+$ or Au$_o^+$ interstitial ion to give an Ag$_3$ or AuAg$_2$ cluster. This is followed by the adsorption of an Ag$_o^+$ ion. In the dry photographic system, this positively charged center introduces a site-directing Coulomb field and a deep trap for a subsequently liberated photoelectron. It desensitizes shallow traps and remaining Ag$_2$ molecules. The Ag$_4^+$ center corresponds to the latent subimage speck of Berg[60,159,160] and to the P-center of Hamilton and Baetzold.[158,172]

In the second effective event, a photoelectron is attracted to and trapped by the latent image growth nucleus and the positive charge is restored by the adsorption of an Ag$_o^+$ ion giving an Ag$_5^+$ or AuAg$_4^+$ development center of minimum size for the aqueous medium. This development center grows by the repetition of these processes. The efficiency of the nucleation and growth process is ensured by the site-directing property for a photoelectron of the positively charged latent image growth nucleus and the development center.

That there is no efficient process for the formation of a cluster of Ag or of Ag and Au atoms at one site during exposure presents a serious problem for the direct photolysis theories.[86] If a developable latent image is to be formed by the occurrence of two to four events at one site, the *first effective* event must create a positively charged center which can attract and trap a photoelectron. After trapping an electron, the trap must be rapidly reset by the adsorption of an Ag^+ ion. This important concept was introduced in 1954 and is an essential feature of the photoaggregation theory. In the initial process of the Hamilton nucleation and growth theory, an Ag atom is produced following the direct trapping of a conduction electron at a very shallow trap provided by an Ag^+ *ion* on a kink site, without the participation of an Ag^+_o ion in the actual trapping process at the trapping site.[163] With the rigorous methods of statistical thermodynamics, it was proved in 1983 that a conduction electron cannot possibly be trapped at room temperature in these circumstances.[134,170]

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References

1. R. L. Maddox, *Br. J. Photogr.* **18,** 422 (1871).
2. J. King, *Br. J. Photogr.* **20,** 542 (1873); *Br. J. Photogr.* **21,** 294 (1874).
3. J. Johnston, *Br. J. Photogr.* **20,** 544 (1873).
4. H. W. Vogel, *Ber. deut. Chem. Ges.* **6,** 1302 (1873); *Phil. Photogr.* **11,** 25 (1874).
5. J. M. Eder, *Sitzber. Kais. Akad. Wiss. Wien.* **90,** 1097 (1884).
6. J. M. Eder, *Photogr. Korr.* No. **361,** 455 (1890).
7. B. Homolka, Ger. Pat. 172,118 (July 29, 1905).
8. A. S. Wortley, *Br. J. Photogr.* **23,** 307 (1876).
9. C. H. Bennett, *Br. J. Photogr.* **25,** 146 (1878).
10. D. E. van Monckhoven, *Bull. Soc. Franç. Photogr.* **25,** 204 (1879).
11. W. de W. Abney, *Photogr. Korr.* **16,** 104, 248 (1879); *Phot. News*, 174, 196 (1880).
12. J. M. Eder, *Sitzber. Kais. Akad. Wiss. Wien.* **81,** 679 (1880).
13. J. M. Eder, *Photogr. Arch.* **22,** 109 (1881).
14. J. M. Eder, *Ausführliches Handbuch der Photographie,* 3rd. ed., Knapp, Halle, 1886.
15. J. M. Eder, *History of Photography,* translated by E. Epstean, Columbia, New York, 1945.
16. G. B. Beccaria, Reference 15, p. 86.
17. C. W. Scheele, Reference 15, pp. 96–97.
18. G. Wetzlar, *Schweigger's J. Chem. Phys.* **25,** 467 (1828).
19. M. Carey Lea, *Am. J. Sci.* **33,** 347, 480, 489 (1887).
20. M. Carey Lea, *Am. J. Sci.* **37,** 476 (1889).
21. R. Abegg, *Arch. Wiss. Photogr.* **1,** 15 (1899).
22. R. Abegg, *Arch. Wiss. Photogr.* **1,** 268 (1899).
23. K. Schaum, *Arch. Wiss. Photogr.* **1,** 139 (1899).
24. K. Schaum, *Arch. Wiss. Photogr.* **2,** 9 (1900).
25. J. M. Eder, *Photogr. Korr.* No. **464,** 276 (1899).
26. J. M. Eder, *Photogr. Korr.* No. **465,** 332 (1899).
27. J. M. Eder, *Sitzber. Kais. Akad. Wiss. Wien.* **114,** 1159 (1905).
28. H. Lüppo-Cramer, *Photogr. Korr.* **44,** 286, 327 (1907).
29. H. Lüppo-Cramer, *Kolloidchemie und Photographie*, 1st ed., Dresden, Steinkopf, 1909.
30. H. Lüppo-Cramer, *Photo. Mitt.* **328** (1909); No. **587,** 397 (1909); No. **588,** 415 (1909); No. **590,** 526 (1909).
31. W. Reinders, *Z. Phys. Chem.* **77,** 213 (1911).
32. W. Reinders, *Z. Phys. Chem.* **77,** 356 (1911).
33. H. Lüppo-Cramer, *Photogr. Korr.* **49,** 118, 501 (1912).
34. H. Lüppo-Cramer, *Kolloidchemie und Photographie*, 2nd ed., Dresden, Steinkopf, 1921.
35. H. Lüppo-Cramer, *Die Grundlagen der photographischen Negativverfahren,* Knapp, Halle, (1927).
36. R. Namias, *Photogr. Korr.* **42,** 155 (1905).
37. G. A. Perley, *J. Phys. Chem.* **14,** 685 (1910).
38. W. D. Bancroft, *J. Phys. Chem.* **14,** 12, 97, 201, 620 (1910); **15,** 313, 551 (1911); **16,** 29, 89 (1912); **17,** 93 (1913).
39. W. D. Bancroft, *Trans. Faraday Soc.* **19,** 243 (1923).
40. P. P. Koch and H. Vogler, *Ann. Phys.* **77,** 495 (1925).
41. S. Arrhenius, *Sitzber. Kais. Akad. Wiss. Wien.* **96,** 831 (1887).
42. Ch. Winther, *Z. Wiss. Photogr.* **9,** 229 (1911).
43. Ch. Winther, *Z. Wiss. Photogr.* **11,** 92 (1913).
44. K. Fajans and K. von Beckerath, *Chem. Z.* 606 (1921).
45. S. E. Sheppard and A. P. H. Trivelli, *Phot. J.* **61,** 400 (1921).
46. H. Kieser, *Z. Wiss. Photogr.* **26,** 321 (1929).
47. C. Tubandt and S. Eggert, *Z. Anorg. Chem.* **110,** 196 (1920); C. Tubandt, *Z. Anorg. Chem.* **115,** 105 (1921); C. Tubandt, *Wien-Harms Handbuch der Experimentalphysik,* **12,** Pt. 1: Akad. Verlag, Leipzig, 1932. pp. 383–469.
48. A. Joffé, *Ann. Phys.* **72,** 481 (1923).
49. J. Frenkel, *Z. Phys.* **35,** 652 (1926).
50. W. Jost, *J. Chem. Phys.* **1,** 466 (1933).
51. E. Koch and C. Wagner, *Z. Phys. Chem. B* **38,** 295 (1937).
52. J. Frenkel, *Kinetic Theory of Liquids*, Oxford, Clarendon Press, 1946.
53. J. Eggert, *Z. Elektrochem.* **32,** 491 (1926).
54. S. E. Sheppard, *Photogr. J.* **65,** 380 (1925).
55. S. E. Sheppard, *Colloid Symposium Monograph,* **3,** 76 (1925).
56. S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland, *J. Franklin Inst.* **200,** 51 (1925).
57. S. E. Sheppard, U. S. Patent 1,574,544, (March 2, 1926).
58. S. E. Sheppard, *Photogr. J.* **68,** 397 (1928).
59. R. W. Gurney and N. F. Mott, *Proc. Roy. Soc. A* **164,** 151 (1938).
60. W. F. Berg, *Rep. Progr. Phys.* **11,** 248 (1948).
61. F. W. H. Mueller, *J. Opt. Soc. Am.* **39,** 494 1949).
62. R. Koslowsky, *Z. Wiss. Photogr.* **46,** 65 (1951).
63. E. J. Birr, *Stabilization of Photographic Silver Halide Emulsions,* Focal Press, London, 1974.
64. K. Fajans, *Z. Elektrochem.* **28,** 409 (1922).
65. W. Frankenburger, *Z. Phys. Chem.* **105,** 273 (1923).
66. K. Fajans, Reference 35, p. 633.
67. S. E. Sheppard and W. Vanselow, *J. Phys. Chem.* **33,** 250 (1929).
68. S. E. Sheppard and W. Vanselow, *J. Phys. Chem.* **34,** 2719 (1930).
69. W. Bodenstein, *Naturwiss.* **28,** 145 (1940).
70. W. Bodenstein, *Abh. Preuss. Akad. Wiss.* **19,** 1 (1941).
71. J. W. Mitchell, *J. Imaging Sci.* **30,** 91 (1986).
72. K. V. Chibisov, *J. Photogr. Sci.* **18,** 73 (1970).
73. K. V. Chibisov, *J. Photogr. Sci.* **21,** 125 (1973).
74. B. H. Carroll and D. Hubbard, *Bur. Stds. J. Res.* **11,** 743 (1933).
75. B. H. Carroll, U. S. Patent 2,487,850 (November 15, 1949).
76. W. G. Lowe, J. E. Jones, and H. E. Roberts, in *Fundamental Mechanisms of Photographic Sensitivity,* J. W. Mitchell, Ed., Butterworth, London, 1951, p. 112.
77. J. F. Hamilton, *Photogr. Sci. Eng.* **14,** 102 (1970).
78. J. F. Hamilton, in *The Theory of the Photographic Process*, 4th ed., T. H. James, Ed., Macmillan, New York, 1977, Chapter 4, p. 105.
79. J. F. Hamilton, *Photogr. Sci. Eng.* **26,** 263 (1982).
80. J. F. Hamilton, in *The Physics of Latent Image Formation in Silver Halides*, Proceedings of an International Symposium, Trieste, Italy, July 11–14, 1983, World Scientific, Singapore, 1984, p. 203.
81. J. F. Hamilton, *Adv. Phys.* **37,** 359 (1988).
82. T. Tani, S. Kikuchi, and K. Honda, *Photogr. Sci. Eng.* **12,** 80 (1968).
83. T. Tani, *Photogr. Sci. Eng.* **13,** 231 (1969).
84. T. Tani, *Photogr. Sci. Eng.* **18,** 165 (1974).
85. T. Tani, *Photogr. Sci. Eng.* **26,** 213 (1982).
86. T. Tani, *Photographic Sensitivity: Theory and Mechanisms,* Oxford University Press, New York, 1995.
87. J. M. Hedges and J. W. Mitchell, *Philos. Mag.* **44,** 223, 357 (1953).
88. T. Evans, J. M. Hedges, and J. W. Mitchell, *J. Photogr. Sci.* **3,** 73 (1955).
89. P. V. McD. Clark and J. W. Mitchell, *J. Photogr. Sci.* **4,** 1 (1956).
90. J. W. Mitchell, *Imaging Sci. J.* **45,** 2 (1997).
91. J. W. Mitchell, *Proc. Roy. Soc., London, A* **371,** 149 (1980).
92. J. W. Mitchell, *J. Soc. Photogr. Sci. Technol. Jpn.* **54,** 248 (1991).
93. J. W. Mitchell, *J. Soc. Photogr. Sci. Technol. Jpn.* **54,** 258 (1991).
94. J. W. Mitchell, *J. Imaging Sci. Technol.* **41,** 1 (1997).
95. J. W. Mitchell, *J. Soc. Photogr. Sci. Technol. Jpn.* **48,** 191 (1985).
96. J. W. Mitchell. *J. Imaging Sci.* **33,** 103 (1989).
97. J. W. Mitchell. *J. Photogr. Sci.* **42,** 2 (1994).
98. J. W. Mitchell, *J. Imaging Sci.* **34,** 217 (1990).
99. J. W. Mitchell, *J. Imaging Sci.* **31,** 239 (1987).
100. J. W. Mitchell, *J. Imaging Sci.* **35,** 341 (1991).
101. J. W. Mitchell, *J. Imaging Sci. Technol.* **37,** 331 (1993).
102. J. W. Mitchell, *Photo. Korr. 1 Sonderheft* 1 1957); *Rep. Progr. Phys.* **20,** 433 (1957).
103. J. W. Mitchell. *Photogr. Sci. Eng.* **27,** 81 (1983).
104. S. Urabe, U. S. Patent 4,897,208 (November 7, 1989).
105. Y. Ichikawa, H. Ohnishi, S. Urabe, A. Kojima, and A. Katoh, U. S. Patent 5,035,991 (July 30, 1991).
106. Y. Suga, M. Kikuchi, M. Yagihara, H. Okamura, and H. Kawamoto, U. S. Patent 5,418,124 (May 23, 1995).

107. M. Kikuchi, and H. Okamura, U. S. Patent 5,498,516 (March 12, l996).
108. M. Kikuchi, M. Yagihara, H. Okamura, and H. Kawamoto, U. S. Patent 5,527,664 (June 18, 1996).
109. J. T. Kofron, R. E. Booms, C. G. Jones, J. A. Haefner, H. S. Wilgus, and F. J. Evans, U. S. Patent 4,439,520 (March 27, 1984).
110. M. Saitou, S. Urabe, and K. Ozeki, U. S. Patent 4,797,354 (January 10, 1989).
111. M. Saitou, U. S. Patent 4,945,037 (July 31, 1990).
112. H. Ikeda, M. Fujita, S. Ishimaru, H. Ayato, and S. Urabe, U. S. Patent 4,806,461 (February 21, 1989).
113. A. Miethe and A. Traube, Ger. Pat. 142,826 (May 6, 1902).
114. W. H. Mills and W. J. Pope, *Photogr. J.* **60,** 183, 253 (1920).
115. W. H. Mills and K. S. Wishart, *J. Chem. Soc.* **117,** 579 (1920).
116. O. Fischer and G. Scheibe, *J. Prakt. Chem.* **100,** 86 (1920)
117. W. H. Mills and F. M. Hamer, *J. Chem. Soc.* **117,** 1550 (1920).
118. W. König, *Ber. deut. Chem. Ges.* **55,** 3293 (1922).
119. W. H. Mills, *J. Chem. Soc.* **117,** 455 (1920).
120. W. König and W. Meier, *J. Prakt. Chem.* **109,** 324 (1925).
121. F. M. Hamer, *The Cyanine Dyes and Related Compounds, The Chemistry of Heterocyclic Compounds,* Vol. 18, A. Weissburger, Ed., Interscience, New York, 1964.
122. W. West, *Photogr. Sci. Eng.* **18,** 35 (1974).
123. J. W. Mitchell, *J. Photogr. Sci.* **5,** 49 (1957).
124. J. W. Mitchell, *J. Photogr. Sci.* **6,** 57 (1958).
125. M. Tamura and H. Hada, *Photogr. Sci. Eng.* **11,** 82 (1967).
126. F. Dorr, in *Die Grundlagen der photographischen Prozesse mit Silberhalogeniden*, H. Frieser, G. Haase, and E. Klein, Eds., Akademische Verlag, Frankfurt-am-Main, 1968, p. 1060.
127. F. Dorr, in *Dye Sensitization*, W. F. Berg, U. Mazzicato, H. Meier, and G. Semerano, Eds., Focal Press, London, 1970, p. 272.
128. J. W. Mitchell, *J. Photogr. Sci.* **40,** 94 (1992).
129. A. Stanienda, *Z. Phys. Chem.* **32,** 238 (1962); *Z. Phys. Chem.* **33,** 170 (1962).
130. R. F. Large, in *Photographic Sensitivity*, R. J. Cox, Ed., Academic Press, New York, 1973, p. 241.
131. J. R. Lenhard, The International East-West Symposium on the Factors Influencing Photographic Sensitivity, October 28–November 2, 1984, Maui, Hawaii, Society for Imaging Science and Technology, Springfield, VA, 1984, p. C 13.
132. P. B. Gilman, Jr., *Photogr. Sci. Eng.* **18,** 475 (1974).
133. J. W. Mitchell. *Photogr. Sci. Eng.* **27,** 96 (1983).
134. J. W. Mitchell, *J. Photogr. Sci.* **31,** 227 (1983).
135. O. Bloch and F. F. Renwick, *Photogr. J.* **60,** 145 (1920).
136. F. F. Renwick and O. Bloch, U. S. Patent 1,372,548 (March 22, 1921).
137. P. B. Gilman, Jr., *Photogr. Sci. Eng.* **18,** 418 (1974).
138. C. E. K. Mees, US Patents 2,075,046-8 (March 30, 1937).
139. J. W. Mitchell, *J. Imaging Sci.* **30,** 102 (1986).
140. W. West and B. H. Carroll, *J. Chem. Phys.* **15,** 529 (1947); *J. Chem. Phys.* **19,** 417 (1951).
141. S. S. Collier, *Photogr. Sci. Eng.* **18,** 430 (1974).
142. P. B. Gilman, Jr., T. L. Penner, T. D. Koszelak, and S. K. Mroczek, in *Progress in Basic Principles of Imaging Systems,* F. Granzer and E. Moisar, Eds., Vieweg, Braunschweig, 1987, p. 228.
143. L. Silberstein, *Philos. Mag.* **44,** 257 (1922).
144. L. Silberstein, *Philos. Mag.* **45,** 1062 (1923).
145. L. Silberstein, *Philos. Mag.* **5,** 464 (1928).
146. L. Silberstein, *J. Opt. Soc. Am.* **31,** 343 (1941).
147. L. Silberstein and A. P. H. Trivelli, *J. Opt. Soc. Am.* **28,** 441 (1938).
148. L. Silberstein, *J. Opt. Soc. Am.* **29,** 432 (1939).
149 L. Silberstein, *J. Opt. Soc. Am.* **32,** 474 (1942).
150. A. E. Ames, *Photogr. Sci. Eng.* **17,** 154 (1973).
151. R. Shaw, *J. Photogr. Sci.* **21,** 25 (1973).
152. M. Kawasaki, S. Fujiwara, and H. Hada, *Photogr. Sci. Eng.* **22,** 290 (1978).
153. L. Silberstein and A. P. H. Trivelli, *Philos. Mag.* **44,** 956 (1922).
154. L. Silberstein and A. P. H. Trivelli, *J. Opt. Soc. Am.* **35,** 93 (1945).
155. J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **30,** 205 (1959).
156. J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **32,** 369 (1961).
157. D. M. Spracklen, *J. Photogr. Sci.* **9,** 145 (1961).
158. J. W. Mitchell, *J. Imaging Sci. Technol.* **39,** 193 (1995).
159. J. W. Mitchell, *J. Imaging Sci.* **31,** 1 (1987).
160. J. W. Mitchell, *J. Photogr. Sci.* **31,** 148 (1983).
161. J. W. Mitchell, *Photogr. Sci. Eng.* **26,** 270 (1982).
162. J. W. Mitchell, *Photogr. Sci. Eng.* **22,** 1 (1978).
163. J. W. Mitchell, *Photogr. Sci. Eng.* **22,** 249 (1978).
164. J. W. Mitchell, *Photogr. Sci. Eng.* **23,** 1 (1979).
165. J. W. Mitchell, *J. Photogr. Sci.* **44,** 82 (1996).
166. M. B. Hodgson, *J. Franklin Inst.* **184,** 705 (1917).
167. T. Evans and J. W. Mitchell, in *Defects in Crystalline Solids*, Physical Society London, 1955, p. 413.
168. S. E. Sheppard, *Photogr. J.* **71,** 313 (1931).
169. J. W. Mitchell, *Sci. J. Roy. Coll. Sci. Lond.* **24,** 19 (1954); J. H. Burrow and J. W. Mitchell, *Philos. Mag.* **45,** 208 (1954).
170. J. W. Mitchell, *J. Imaging Sci.* **34,** 113 (1990).
171. J. W. Mitchell, *Photogr. Sci. Eng.* **25,** 170 (1981).
172. J. F. Hamilton and R. C. Baetzold, *Photogr. Sci. Eng.* **25,** 189 (1981).