CHIMIA

Volumen 22 Fasc. 9 1968 Pag. 353–384

The Mechanism of Chemical Sensitization of Photographic Silver Halide Emulsions*

By **Fritz Dersch**

GAF Corporation, Photo & Repro Division, Binghamton, New York

Abstract

After an introduction giving a brief history of discoveries of chemical sensitization of photographic silver halide emulsions, the general role of all types of chemical sensitizers is given. This includes a description of chemically and non-chemically sensitized silver halide crystals, the functions of chemical sensitizers, the end products of chemical sensitization and their functions.

The mechanisms of the different types of chemical sensitization (sulfur, reduction, noble metal and combinations of these) are discussed.

I. Introduction

The photographic emulsion is normally prepared in a precipitation process, that is, an aqueous silver nitrate solution is added to an aqueous solution of halides and gelatin. During and after the silver nitrate addition, a growth of silver halide crystals takes place, which is enhanced by the presence of silver halide solvents such as potassium bromide or ammonia. This part of the process is called physical or **Ostwald** ripening. The sensitivity of the silver halide crystals to light generally increases with their size, but in order to reach the maximum sensitivity, the photographic silver halide emulsion has to be digested after removing the silver halide solvents by washing. This part of the process during which the emulsion is heated for a certain lenght of time is called second ripening, chemical ripening or afterripening. During this process, chemical sensitization (222) of the photographic silver halide emulsion takes place. It differs from the physical ripening (223) in that it has no effect on the crystal growth. Under certain conditions (1, 2), the sensitivity to light can be extended to longer wavelengths than that of the intrinsic sensitivity to UV and blue light.

Spectral sensitization (i.e., the method to increase the sensitivity of silver halide to light of longer wavelengths by adding sensitizing dyes) will not be discussed in this article. There is no evidence (175) that spectral sensitivity is influenced by chemical sensitization, both sensitizations being additive (176, 177, 178, 228).

When gelatin was introduced as a binder for photographic silver halide emulsions by **Maddox** in 1871, chemical sensitization was unknowingly invented. When **Sheppard** (3) isolated sulfur compounds from gelatin 40 years later, the importance of sulfur sensitization was realized. In 1931, **Carroll** and **Hubbard** (4) pointed to the reduction of silver halide to silver as the origin of sensitivity nuclei. The term «reduction sensitization» was introduced by **Lowe**, **Jones** and **Roberts** (5) in 1951. Thirty-three years ago, gold sensitization was discovered by **Koslowsky** (6) when he studied the effect of aurous complexes during the chemical ripening on light sensitivity. With this discovery, a new era in silver halide photography began. Photographic emulsions with higher sensitivity and finer grain were made possible and intensive work on the mechanism of chemical sensitization was pursued in many laboratories.

A discussion of mechanisms of chemical sensitization serves several purposes. First, it is necessary to gain an understanding of each part of this complicated system. The danger of over-simplifiying the explanations of the various effects of chemical sensitization has to be overcome and a deeper understanding, with the help of the tools of solid state physics and chemistry, has to be reached. The next step is the elucidation of the mechanisms of the combined effects of the different types of chemical sensitization.

II. Discussion

A. *Theory and Functions of the Products of Chemical Sensitization During Exposure*

According to the "concentration-speck theory" by **Sheppard**, **Trivelli** and **Loveland** (20), products of the chemical sensitization, silver and/or silver sulfide, called "sensitivity specks", concentrate upon exposure to radiation the photolytic products, i. e., silver ions form minute particles of silver, which are called "latent image specks." These act as nuclei for the catalytic reduction of silver halide during development. While this theory was useful for over ten years, it is now considered inadequate.

In 1938, **Gurney** and **Mott** (12a) advanced the following theory. When the silver halide crystal is struck

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* Received June 24, 1968.

by light, the absorption of the light quanta causes the release of electrons from the bromide ions. These photoelectrons are trapped by the "sensitivity specks" which obtain a negative charge. Interstitial positive silver ions available in the crystal in a thermo-dynamic equilibrium move to these negatively charged specks and, in neutralizing them, form silver atoms, composing the latent image. The positive holes (bromine atoms) play no important part in the original GURNEY-MOTT theory.

This theory satisfies many aspects of photographic sensitivity [BERG (13)]. It also stimulated much research work, on the basis of which it was modified and supplemented.

MITCHELL (14, 15, 16, 18), in particular, proposed a theory which differed in several respects. He stressed the importance of the existence of structural imperfections and dislocations inside and on the surface of the silver bromide crystal (17), which he called "sensitivity centers." The products of chemical sensitization, e.g., silver sulfide, may be deposited on those reactive sites. Silver sulfide has two functions: to increase efficiency of sensitization, that is, attract and stabilize silver atoms and to act as an acceptor for positive holes.

Upon exposure to light, the following sequence of events was proposed by MITCHELL. Photo-electrons are liberated from the light-absorbing bromide ions. The electrons and the interstitial silver ions combine to form the latent image specks at sites adjacent to surface silver ions on kink and edge sites on the external surface, on jog and edge sites along internal dislocations or near a silver sulfide speck. Then (after the absorption of a second quantum) two bromine atoms combine to form neutral halogen molecules which can diffuse away from the surface or are trapped by a silver sulfide molecule on the surface. It is the function of silver sulfide to provide more numerous traps for these positive holes and thus protect the silver specks from recombination with bromine which would annul the photolytic reaction product.

This dual function of silver sulfide was demonstrated by MITCHELL (36) as follows: A silver bromide macrocrystal, sensitized with sodium thiosulfate, was exposed to light through a 1 mm wide slit. Upon development of the crystal in a surface developer, a dense black image of the slit was obtained. A similarly sensitized and exposed but not developed piece of the same crystal was treated with dilute chromic acid solution in order to oxidize the surface latent image in the slit area. This crystal was washed and dried and then uniformly exposed to the same light source and developed in a surface developer. This time, the slit area remained clear while the adjacent areas which had received only the second uniform exposure developed to black silver.

The results of this experiment could lead to the conclusion that the silver sulfide plays an important part during the first exposure, probably trapping positive holes and releasing silver ions:

$$Ag_2S + \text{positive hole} = AgS + \text{silver ion}$$

The diatomic molecules AgS, not being stable, might dissociate into silver atoms and sulfur atoms, these being in turn oxidized by the chromic acid solution at a higher rate than the silver sulfide. Some of these considerations are based on the assumption that in solid state surface chemistry the stoichiometric rules of classical chemistry are not necessarily obeyed.

Thus, according to the GURNEY and MOTT theory, the products of chemical sensitization are the trapping centers for the photo-electrons and according to MITCHELL they are the trapping centers for the positive holes. A compromise between the two principles has recently been suggested by BERG (225) and also by MALINOWSKI (229). BERG proposed that the natural trapping sites for electrons are structural defects whereas those for the positive holes are impurity ions in the crystal or on its surface. MALINOWSKI pointed to the formation of silver atoms upon the neutralization of trapped electrons by interstitial silver ions and to the supposition that sensitizers act as bromine acceptors and not as hole traps.

HAYNES and SHOCKLEY (22a, b) demonstrated the participation of photo-electrons in the photographic process when submitting an AgCl crystal in a pulsed electric field to a strong light exposure. They could show that photolytic silver is formed near the anode, thus demonstrating the mobility of photo-electrons in the crystal.

WEBB (23) and later HAMILTON, HAMM and BRADY (24) also exposed silver bromide grains in pulsed electric fields. They showed the liberated electrons drift in the electric field to be concentrated near the electrically positive side (anode) of the grain and also a reduction of silver ions to silver in the same region. A cloud of brominated gelatin appeared on the cathode side, thus indicating also a mobility of the positive holes, i. e., the bromine atoms, most likely by a charge exchange of halide ions and atoms adjacent in the crystal lattices.

KLEIN and MATEJEC (25a, b, c) conducted experiments in a steady electric field and showed the participation of interstitial silver ions in the primary photographic process. The interstitial silver ions moved towards the cathode.

WEST (26) showed the effects of a sulfur sensitizer, e.g., allyl thiourea on photoconductivity and on photographic sensitivity. Upon digestion, in the presence of a sulfur sensitizer, which presumably leads to the formation of silver sulfide, sensitivities of ten times that of the unsensitized emulsion could be observed. Simultaneously, the magnitude of the photocurrents was reduced, which could be attributed to the action of Ag_2S as deeper electron traps, in agreement with the theories by SHEPPARD, TRIVELLI and LOVELAND (20) and GURNEY and MOTT (12b).

HAMILTON and BRADY (28a, b, c) made conductivity measurements on the grains of a photographic emulsion by employing flash exposures in pulsed electric fields and found that mobile silver ions are instrumental in the initial trapping of photo-electrons. They assumed that all electron traps are very shallow and that the electron is immobilized by its combination with a mobile silver ion. Lifetimes of positive holes were found to be ten times longer than those of electrons. Indications are that hole mobility is considerably lower than that of electrons, which was shown by **Malinowski** and **Süptitz** (30).

With regard to the function of the product of reduction sensitization (silver atoms) during exposure, **Matejec** (19) took the view that these silver specks adsorbed interstitial silver ions to become positively charged.

The following equations represent the present status of our knowledge of the role of the products of chemical sensitization during the formation of the latent image:

$$\begin{array}{l}\text{primary}\\ \text{quantum}\\ \text{absorption}\end{array} \quad Ag^+ + Br^- + h\nu \rightarrow Ag^+ + Br^0 + e^- \qquad (1)$$

a) For reduction-sensitized silver halide crystal:

$$Ag_{\text{sensitivity speck}} + Ag^+_{\text{int}} + e^-_{\text{photolytic}} \rightarrow Ag_2 \qquad (2)$$

(1) and (2) can be repeated for each quantum absorbed, thus enlarging the size of the latent image speck.

b) For sulfur-sensitized silver halide crystal:

$$Ag_2S_{\text{sensitivity speck}} + \underset{\substack{\downarrow \\ \text{from primary quantum} \\ \text{absorbed (see [1])}}}{\text{(positive hole)}} \rightarrow AgS + Ag^+ \qquad (3)$$

The Ag^+ in (3) can either combine with a reduction-sensitized Ag atom according to (2) to form Ag_2^+ which, after absorption of a second quantum, forms a Ag_2 sub-latent image speck.
Or, the Ag^+ in (3) can combine directly with the photolytic electron formed in the primary quantum absorption to form Ag_0.

When silver halide is exposed to light, photo-electrons and positive holes are formed. The positive holes, which are identical with halogen atoms, are removed by halogen acceptors at the crystal surface, such as Ag_2S or by other halogen acceptors at the surface. The photo-electrons react with interstitial silver ions to form silver atoms, first as latent silver nuclei (latent image) and finally as visible photolytic silver.

B. *The Mechanism of Chemical Sensitization in Presence of Photographic Gelatins*

The study of the mechanism of chemical sensitization of silver halide in "active" photographic gelatins is complicated by the presence of many "impurities" in the gelatin. Depending on their origin and method of manufacture, these gelatins contain a mixture of active compounds such as sulfur sensitizers, reduction sensitizers, fogging substances and restrainers (39, 42, 43, 109, 117, 142, 143, 145, 146, 222). Restrainers are compounds which can restrain crystal growth by being adsorbed on the grain and which can also restrain chemical ripening (222) for the same reason or because of their abilitiy to complex silver. They can also, by the same mechanism, restrain the formation of fog. Fog is caused by excessive chemical ripening, whereby developable silver is produced without exposure. Examples of restrainers are nucleic acids and their decomposition compounds such as purines and pyrimidines, e.g., adenine. Methods to determine their amounts in gelatine were recently worked out by **Russell** and **Oliff** (205 a and b).

The classical theory of the mechanism of chemical sensitzization, advanced by **Sheppard**, **Trivelli** and **Loveland** (20), originated at a time when only "active" photographic gelatins were used in commercial photographic emulsions. According to this theory, minute quantities of sulfur compounds contained in the gelatin and later identified to be mainly sodium thiosulfate (37) give rise to sulfur sensitization, i.e., the formation of silver sulfide. The importance of the reducing agent Na_2SO_3 present in active gelatin was shown by **Carroll** and **Hubbard** (38), leading to the formation of silver nuclei, which is the basis of reduction sensitization.

The study of the mechanism of chemical sensitization became even more difficult with gold sensitization (i. e., the speed increase when using gold salts in the chemical ripening stage) in the presence of active gelatin because of the reaction of the gold salts with the impurities in the gelatin and because of the complexing of gold by gelatin (41). **Steigmann** (40) reported a stronger complexing of gelatin with palladium than with gold so that it could be expected that, in the presence of palladium, more efficient gold sensitization is possible.

C. *Model Experiments*

A better understanding of the mechanism of chemical sensitization can be gained when studying the behavior of silver halide crystals in the absence of gelatin or of the gelatin impurities.

a) *Chemical Sensitization on Crystals*

Evans, **Hedges** and **Mitchell** (44) contributed greatly to a better knowledge of the chemical sensitization by conducting their experiments with large strained and unstrained (after annealing) crystals of silver bromide. After exposure to light, no developable surface latent image with unsensitized strained crystals was obtained, but a latent image in the interior of the crystal (internal latent image) could be demonstrated. Then various methods of chemical sensitization, reduction, sulfur (by bathing in $Na_2S_2O_3$) and gold were applied. All three methods gave developable surface latent images.

Sensitization was also observed when digesting a crystal in a ½% solution of inert gelatin (a gelatin from which the active compounds had been removed) at moderately high temperature, preferably at pH of 3.5 to 8.5 and between p_{Ag} 3.5 to 8.5. This type of sensitization was attributed to the adsorption of silver ions and OH ions on the crystal, as WOOD (127, 128) had also observed in regular emulsions. Sensitization was obteined when the crystal was immersed in a highly diluted aqueous gelatin solution containing small amounts of thiosulfate. In this case, the maximum attainable sensitization was also dependent upon the concentrations of silver and hydroxyl ions in the gelatin.

Interesting were the experiments in which the stability of thin films of silver, gold and silver sulfide on silver bromide crystals were determined: Thin films of silver condensed on the crystals by vacuum deposition are not stable; the silver will disappear on storage. Dissolving these deposits with KCN, one will find that the silver has diffused into the crystal, but gold and Ag_2S will remain on the surface of the crystal. The silver which had disappeared from the surface of the crystal will appear again as internal fog ($= Ag^0$), when treating such a crystal with a solution of chromic acid and then with an internal developer containing silver halide solvents such as $Na_2S_2O_3$. If, however, this experiment was repeated with a crystal which had been also sensitized with silver sulfide by treatment with a dilute solution of sodium thiosulfate, no internal fog could be detected. This was explained by the function of silver sulfide to stabilize the silver atoms, silver sulfide adhering strongly to silver bromide possibly forming an adsorbed monolayer and thus holding the silver on the surface.

b) *Chemical Sensitization in Inert Gelatins*

The use of inert gelatins became a suitable medium to study the mechanism of chemical sensitization. Inert gelatins are those which contain practically no chemical ripeners, such as sulfur compounds or reducing substances, and little or practically no restrainers. AMMANN (45) designed a physical method to distinguish active gelatins containing both ripeners and restrainers and inert gelatins. In this method, the effect of increasing concentrations of gelatins during increasing times on the grain growth of silver chloride grains is determined by measuring the change of turbidity which is a measure of crystal size (for crystal sizes smaller than approximately 0.25 μ). The turbidity values are plotted against gelatin concentration with ripening time as a parameter. An inert gelatin, having little effect on grain growth, will give a group of parallel, horizontal lines.

Methods for deactivation, i.e., removing chemical ripening and restraining properties, of gelatins for photographic use were described by AMMAMNN (46, 142), KELLY (47), and CROOME and CLEGG (48). Inert gelatins with good physical properties, such as gel strength, setting point, melting point, viscosity, are now manufactured, using carbon treatment, ion exchange and control of liming.

KELLY (47) showed that sodium sulfite alone is a weak sensitizer for inert gelatin. Higher sensitivities can be obtained with sodium thiosulfate. The optimum sensitization for inert gelatin, practically reaching the sensitivity obtainable with the original active gelatin, is accomplished by using sodium sulfite and sodium thiosulfate. It appears that these sensitizers have a synergistic ripening effect.

c) *Comparison of Ripenings in Carrier-Free Suspensions and in Gelatins*

Comparing chemical sensitization in binder-free silver halide suspensions (prepared by slow sedimentation of silver halide and resuspension in water without gelatin) and in silver halide emulsions prepared in gelatins, FAELENS (49) obtained interesting results. He found that, in the presence of gelatin, the chemical ripening with $Na_2S_2O_3$ is considerably retarded; raising the temperature by as much as 20°C is needed to reach the same speed as obtained in a gelatin-free suspension. FAELENS attributed this retardation of the ripening rate to the presence of restraining groups in gelatin (histidine, lycine and arginine) which complex silver ions and consequently counteract the formation of Ag_2S.

By comparing ripenings of silver halide suspensions without gelatin with those in gelatin, FAELENS (50) also found a remarkable difference in the efficiency of noble metal sensitization. In suspensions, he could readily sensitize with gold, platinum and palladium salts. In the presence of gelatin, however, he no longer observed any sensitization with platinum and palladium salts, and the sensitization with gold salts was reduced. This is explained by the stronger complexing power of the gelatin to these metals. Sodium thiosulfate will extract the gold ions from the gelatin by forming a gold complex, which is then adsorbed on the silver halide crystal. This will bring about a more efficient gold sensitization.

D. *Advanced Concepts Leading to Theories on the Latent Image*

a) *Structural Imperfections in Silver Halide Crystals*

One cannot discuss chemical sensitization without considering lattice defects in the silver halide crystals. One has to distinguish between natural and artificial defects (52, 56). The natural defects are those which occur in the silver halide crystal *per se*, such as FRENKEL defects (= interstitial Ag-ions), SCHOTTKY defects (vacant silver ion lattice sites), kink sites and jogs. They are most likely introduced during crystal growth, and their number is in thermodynamic equilibrium at any temperature. The artificial defects are caused by the introduction of elements other than silver and bromine, e.g., iodine, cadmium, lead or copper. They can lead to considerable distortions and dislocations and stresses in the crystal (53, 55, 57, 63, 64, 111, 215), as does also sulfur.

Mitchell (112) demonstrated well-defined imperfections on surfaces of silver bromide crystals by producing silver upon prolonged exposure (printing out silver). This photolytic silver had separated within the crystal along imperfection and dislocation sites. Mitchell (36) found also that dislocations in silver halide crystals decrease when they are annealed in an atmosphere of halogen between 150–250 °C. This reduces the capacity of the crystal for chemical sensitization.

Since crystal imperfections and dislocations are intimately connected with crystal growth and crystal shape, a thorough study of these in relation to chemical sensitizing is of great importance (57). Silver bromide microcrystals are precipitated in the form of cubes or octahedra. Cube surfaces and octahedral surfaces differ from one another in that the octahedral surfaces are occupied by either silver ions or bromide ions, while cubic faces contain both ions side by side.

Irregular crystal forms in photographic emulsions can frequently be explained by twinning rather than dislocation (58, 59). It is possible that severe dislocations accompany the twinning (17, 60). It is also known that coalescence can exist among crystals, leading to internal disorder (61). Also, chemical ripening differs in different crystal forms. This could be shown by Moisar (62 a, b and c) who could sensitize the cube-faced [100] and steplike octahedral-faced [111] crystal to a different degree. He found a difference in the extent of sulfur sensitization on octahedral crystals ([111] surfaces) and on cubic crystals ([100] surfaces). These observations lead to the suggestion to prepare photographic emulsion with controlled uniform crystal structure in order to obtain certain desired properties. These so-prepared emulsions may also add to a better knowledge of the mechanism of chemical sensitization.

b) *Topography of Sensitization Nuclei*

One can discern between the internal and external latent image using a technique described by Berg, Marriage and Stevens (164, 165): After exposure, development in a surface developer (not containing silver halide solvents) reveals only the surface latent image. Destroying the surface latent image after exposure in an oxidizing bath before development, followed by washing and development in a developer containing a silver halide solvent will yield the internal image.

Consequently, one has to discern also between internal and external sensitivity. Chibisov (220) studied surface and internal sensitivity and he found:

1. Chemical ripening influences both the external and the internal sensitivity, the external sensitivity becoming higher with ripening.
2. Oxidizing photographic layers before exposure to light with 0.25% chromic acid anhydride solution reduces both the external and the internal sensitivity. The external sensitivity can be partially and the internal sensitivity can be fully regenerated by hypersensitization in a triethanolamine solution.

Chibisov (52) studied the changes of internal and external sensitivity during the chemical ripening in presence of hydrazine, a reduction sensitizer, and thiourea, a sulfur sensitizer. Whereas the internal sensitivity remained unchanged, the external sensitivity went through an optimum when increasing the concentration of the two chemical sensitizers. Stevens (166) showed that most of the grains of indigested emulsion carried only internal image but that normally-sensitized emulsion at normal exposure levels formed also a surface image, the duration of the ripening influencing the internal and external sensitivities. The ratio of surface to internal sensitivity depends on the method of chemical sensitization used. Sulfur sensitizing will decrease internal speed and increase surface speed (93 c, 101 b). Reduction (5) and gold sensitization (93 c) will increase both internal and external sensitivity. Mixed sensitization (gold, sulfur and reduction), also prolonged afterripening (167, 168), will lead to higher surface and lower internal sensitivity. But a high ratio of internal to surface image can be found in emulsions with a high silver iodide content (169 a und b). No internal image is found in pure silver iodide emulsions (170). When impurities were introduced into a crystal in a model experiment in the form of a sandwich layer between two sheets of silver bromide, it could be demonstrated (67) that these impurities affect latent image formation according to their ability to trap electrons or positive holes, e.g., ammonium chloroiridite which is known to trap positive holes, enhances the formation of an internal latent image.

c) *Iodide, Silver, Silver Sulfide and Gold Sulfide as Hole Acceptors*

The iodide ion can act as a hole trap, because of its lower e^--affinity than that of Cl^- or Br^-, thereby functioning like a "sensitizer" (54, 65). The ability of silver sulfide to trap positive hole was demonstrated by Mitchell (36) in his slit experiment (see Paragraph A, page 354).

This trapping of positive holes by silver sulfide is an important function during latent image formation (7, 8, 36, 53, 66) and will prevent the rebromination of silver atoms on the crystal surface

$$Ag^0 + Br^0 \rightarrow AgBr$$

which otherwise would take place and cancel out the photolytic products.

Another medium which can serve as a trap for positive holes is the product of gold and sulfur sensitization:

$$Au_2S + \text{positive hole} = AuS + \text{aurous ion}$$

Still another substance which Mitchell (36, 44) found to serve as an excellent trap for positive holes is silver chloroiridite. When thin sheets of silver halide crystals were immersed in a weak solution of potassium or ammonium chloroiridite, they were strongly sensitized. The trapping of positive holes may proceed according to the following scheme:

$$(Ag^+)_3\,(IrCl_6)^{3-} + \text{positive hole} = (Ag^+)_2\,(IrCl_6)^{2-} + Ag^+$$

West and Saunders (67) confirmed the positive hole trapping by a sensitizing layer of silver chloroiridite in otherwise not chemically sensitized silver halide crystals.

Platikanowa and Malinowski (35) studied the fate of positive holes in silver bromide. The bleaching of a silver deposit by photo-excited positive holes drawn to the crystal surface by potential pulses can be used to determine the drift mobility of positive holes. Finding a measurable permeability of these in flat, heavily deformed crystalline sheets of silver bromide (careful annealing completely destroys the positive hole photo response of the crystals), they concluded that dislocations did not act as efficient hole traps, as in the case with electrons. They concluded further that the trapping centers for holes are different from those of electrons. Those positive holes which are not trapped internally reach the surface of the crystal and liberate atoms or molecules of bromine. It is then concluded that the formation of a stable surface speck of silver, the latent image center, is only possible in the presence of an efficient bromine acceptor, such as a chemical sensitizer. This agrees with Hedges and Mitchell's (7) findings that a surface latent image was found only on crystals which were chemically sensitized.

d) *Low and High Intensity Reciprocity Law Failure*

Practically all silver halide emulsions show reciprocity law (Bunsen-Roscoe) failure (29d), i.e., the photo product, the developable silver, cannot be simply determined by the total exposure, the product of intensity I and time t ($I \cdot t$). A photolytic inefficiency exists in extreme regions of exposure, at very short and very long exposure times. The respective phenomena are called low intensity reciprocity law failure (LIRF) and high intensity reciprocity law failure (HIRF).

The mechanism of reciprocity failure is complicated or even uncertain and it has to be connected with a number of events. In the case of low intensity reciprocity law failure (29d), i.e., when the photons arrive at a very time delayed rate, the first event may be the thermal decomposition of a photolytically formed Ag-speck, e.g., Ag_3; $Ag_3^0 \rightarrow Ag_2^0 + Ag^0$ leading to an unstable system before the next active photon is absorbed, which would have regenerated a stable speck. A photolytic inefficiency may also be derived from a reaction of silver atoms with mobile holes, i.e., halogen (Berg, 82).

Mechanisms of high intensity reciprocity law failure (29d) were proposed by Mott and Gurney (74) and Berg (75). Basically, the inefficiency is due to the mobility difference of the silver ions and the electrons in reaching the sensitivity specks. The electrons having a much higher mobility will form a negative charge and will repel further electrons before all the silver ions arrive. These so-repelled electrons are lost for latent image formation; they recombine with positive holes to form Br^- ions (173). Also, the latent image silver may be produced in a more dispersed form, thus becoming less efficient as nuclei for the development, which is a cause of high intensity reciprocity failure.

The theories on chemical sensitization may receive some support from the study of reciprocity law failure. Extensive studies were conducted by Hautot (93d).

A non-chemically sensitized emulsion has a great low intensity reciprocity failure, presumably on account of the instability of the latent image silver nuclei. This low intensity failure is reduced by all kinds of chemical sensitization (16, 69, 70, 71, 72, 174): sulfur, reduction, combination of both, gold chloride, ammonium aurous dithiocyanate, because in these cases more stable, larger and less dispersed silver nuclei (latent image) are formed.

Although a primitive (non-chemically sensitized) pure silver bromide emulsion has no high intensity failure (HIRF, 93d), even when sensitized with reducing substances or gold sensitizer, high intensity failure occurs as soon as iodide is introduced into the silver bromide or when pure bromide or mixed silver-bromide-iodide emulsions are sulfur sensitized, e. g., with $Na_2S_2O_3$ or active gelatin. The effect of iodide in this respect is still debatable.

Hautot (172) assumed that sulfur sensitization reduces either the concentration or the mobility of interstitial silver ions in silver bromide grains, thus producing reciprocity law failure.

Spencer and Atwell (114b) found that very small amounts of sulfur do not produce HIRF but that high concentrations of sulfide ions will produce HIRF.

They postulate that sulfur sensitization may change the localized silver ion properties around the sulfide center on the grain or the electron trapping properties of the grains so that HIRF is introduced. James and coworkers (76), also Spencer and Atwell (114b) found that gold latensification (see page 364) removed HIRF. They also reported that extended development will diminish but not remove HIRF.

HIRF was slight in a case where the amount of sulfur sensitization and the amount of gold sensitization were high, the gold apparently acting similar to its behavior in latensification. Spencer and Atwell (114b) concluded that "the degree of HIRF in a gold plus sulfur-sensitized bromide emulsion is a function of the relative concentration of the sulfur sensitizer and the accompanying gold sensitizer used."

e) *Solarization*

Solarization (29e) is decreasing developability of silver halide emulsions, which have received an extremely high degree of exposure to light. This can be graphically illustrated in a diagram (see curve in reference 29f) in which density and log E ($E = I \cdot t$; where I is light intensity and t is time of exposure) are plotted. Increasing exposure will lead to an S-shaped curve, in which the lower part is called the "toe", which is followed in an upward direction by a "straight-line portion" and which ends at the top with the "shoulder," reaching there the limit of developable density (maximum density).

If a photographic emulsion is exposed to higher light intensities, the developed density does not increase any more but will decrease and the curve will show a downward slope, indicating decreased developed density. This phenomenon (solarization) is also referred to as "reversal." Also, chemical prefogging methods are known (77a, b, c, 87) to bring a normal silver halide emulsion to a condition (resembling the shoulder region in the diagram) at which a strong exposure to light will lead also to a reversal.

Solarization can be best explained by the rehalogenation theory according to which photolytic halide reacts with the surface latent Ag image. The rehalogenation theory first proposed by Hurter and Driffield (80) and Lüppo-Cramer (81), and further elaborated by Berg, Marriage and Stevens (164) and Farnell and co-workers (68) can be supported by the fact that addition of halogen acceptors such as nitrite to the emulsion before exposure will reduce or eliminate solarization (78, 203).

Rebromination was demonstrated by Berg (82) who showed that photolytic bromine, produced by very low intensity exposures, is capable of desensitizing neighboring exposed emulsion areas, producing there a white band (i.e., lower amount of reduced silver) upon further general exposure.

Further support of the rehalogenation theory was given by the experiments with silver bromide crystals which were conducted by Mitchell and co-workers (7, 9, 17, 66). They concluded that, during exposure, the photolytic halogen, after having reacted with the silver sulfide, will also react with the surface latent image.

Klein and Wagner (217) re-emphasized this theory when stating that after the consumption of the halogen acceptor, the positive holes will outnumber the electrons and the photolytic silver will be rehalogenated.

Solarization is mainly connected with the surface latent image, as shown by Hautot and Sauvenier (83) who found no solarization in an internal developer after the surface latent image was removed.

Chemical sensitization will influence the degree of solarization (96). This can be concluded from the fact found by Meidinger (78) that an unripened emulsion did not solarize whereas chemically ripened emulsion showed a strong reversal. The tendency of an emulsion to solarize is enhanced by the presence of silver iodide (79).

According to Hautot (93e), physical ripening has a greater effect on solarization than chemical ripening, the tendency to reverse increasing with grain growth (217). Meidinger (78) had also reported that grain growth produced solarization.

Sulfur-sensitization tends to suppress solarization (202), possibly by providing more hole traps (66, 217). Ripening of silver halide emulsion or bathing with gold salts before or after exposure does not change their tendency to solarize (135).

f) *Herschel Effect*

The destruction of the latent image by red light, i.e., red light exposure before development, is called the Herschel effect (89, 90, 91, 163, 171, 216). A plausible mechanism for this effect was proposed by Gurney and Mott (12a) and is expressed by the following equation:

$$h\nu + \mathrm{Ag}_n \rightarrow \mathrm{Ag}_n^+ + \mathrm{e}^- \rightarrow \mathrm{Ag}_{n-1} + \mathrm{Ag}_{\mathrm{int}}^+ + \mathrm{e}^-$$

A minute silver speck surrounded by silver halide will absorb a light quantum $h\nu$. An electron is ejected into the conduction band of the silver halide, leaving the silver speck positively charged and leading to the loss of a silver atom as an interstitial silver ion. There exists a relationship between the size of the latent image specks and the Herschel effect, the larger image specks being destroyed more slowly by the Herschel exposure.

It is not surprising, therefore, that increasing the size of latent image specks by latensification (see page 364) or by low intensity post exposure will reduce the Herschel effect (92). Latensification (see page 365) with mercury or gold can even eliminate it (92).

In this connection, it is also significant that high-intensity exposures leading to a more dispersed and less stable latent image are more susceptible to the Herschel effect than low intensity exposures. This relationship was studied by G. Kornfeld (73).

The Herschel effect is reduced in gold sensitized emulsion (92, 93a) presumably because of a stabilization of the latent image speck.

Sulfur sensitization has been reported to increase the Herschel effect (93a, 94) which can be explained as follows: The sulfur sensitization promotes trapping of electrons and interstitial silver ions, thus facilitating the dispersion of the latent image (93a).

Commercial products (Autopositive) have been developed utilizing the basic principles of the Herschel effect (86a, 86b, 201). In the presence of certain desensitizing dyes, this reversal is especially effective. These dyes very often induce the reversal in their absorption band. In this specific case, the reversal is called the spectrally-sensitized Herschel effect. This system is also commercially applied for document copying (86a and b).

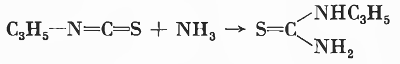
Carroll and Kretchmann (84, 85) attributed the spectrally-sensitized Herschel effect to an oxidation, and Blau (88) showed indeed that oxygen is necessary to obtain reversal, e.g., with pinakryptol yellow.

E. *Mechanism of Sulfur-, Reduction-, and Gold-Sensitization*

For a better understanding of the mechanism of chemical sensitization, it is necessary to deal in more detail with the different types of chemical sensitizations and their inter-relations with each other.

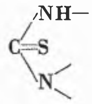
a) *Sulfur Sensitization*

In 1925, Sheppard (3) isolated sulfur compounds from gelatin and from certain stages in the manufacture of gelatin. These were identified as allyl isothiocyanate or allyl thiocarbamide. The effective sulfure sensitizer was believed to be obtained according to the following equation:



$$C_3H_5{-}N{=}C{=}S + NH_3 \rightarrow S{=}C\begin{matrix}NHC_3H_5\\NH_2\end{matrix}$$

It was found that organic compounds of the general structure



can act as sensitizers.

While Sheppard emphasized the presence of isothiocyanates in photographically active gelatins, he included also sodium thiosulfate as a sulfur sensitizer in his basic patent (97).

Steigmann (39, 98a, b, c) reported thiosulfates to be present in photographic gelatins and also studied the addition of these to inert gelatins. Steigmann's findings were confirmed by Krummenerl (99), Wood (37) and Russell (100a and b).

Beersmans and Borginon (117), and also Timson, Kliem, Steigmann and Kelly (144), gave a good review of methods to determine chemical sensitizers (115, 116) and restrainers.

There seems to be general agreement in the literature (101a and b, 102, 103, 104, 105, 106, 107, 108, 109a and b, 110) that silver sulfide is produced during chemical ripening. Lorenz (111) observed the formation of silver sulfide from silver nitrate and labile sulfur containing compounds in a ½% gelatin solution at different *p*H values. He found the Ag_2S formation with thiosulfate independent of *p*H and temperature, pointing to the best suitability of this compound as a sulfur sensitizer.

Mitchell (112) visualizes the reaction of sodium thiosulfate with silver halide as follows:

$$S_2O_3^{--} + 2\,AgBr \rightleftharpoons Ag_2S_2O_3 + 2\,Br^-$$
$$Ag_2S_2O_3 + OH^- \rightleftharpoons Ag_2S + HSO_4^-$$

The thiosulfate ions are adsorbed to the surface of the silver bromide crystal and bromide ions pass into solution. The adsorbed molecules of silver thiosulfate react with OH ions to form molecules of silver sulfide. The silver sulfide is attached to the surface of the crystal.

There does exist condiderable disagreement, however, regarding the mechanism of sulfur sensitization.

On the basis of the slit experiment described earlier (page 354), Mitchell points out the dual role of Ag_2S during latent image formation: 1. the trapping of positive holes, and 2. the attracting of silver atoms and/or ions.

Hickman (21) had proposed two reactions according to which silver sulfide could react with bromine formed besides silver during exposure:

1. $2\,Br + 2\,Ag_2S \rightarrow 4\,Ag + S_2Br_2$
2. $2\,Br + Ag_2S \rightarrow 2\,AgBr + S$

These reactions were theoretically and experimentally supported by Mitchell (7, 44).

Spencer, Brady and Hamilton, and also Spencer and Atwell (114a and b) found that the centers produced by sulfur sensitization affect the distribution of the latent image silver. They concluded that the centers act as nuclei for the growth of the latent image presumably by increasing the depth of electron traps.

According to Hautot (93f), the sulfur sensitization may be explained by the following mechanism. Initially, bromide ions on the surface of the silver bromide crystal are substituted by sulfur ions causing considerable strain on the crystal. Some of these sulfur ions will cede electrons to silver ions and form silver atoms on the surface.

Chibisov and his collaborators (118, 119, 120) concluded from analytical and spectrophotometric data obtained by Kirillov and Broun (121, 122, 123) that in the main mechanism, in which labile sulfur compounds were involved, silver sulfide acted only as a catalyst for reduction of silver ions, forming silver specks as the sensitizing product. This conclusion was based on the observation of numerous absorption bands generated by exposure in silver halide crystals.

Moser (124) could not confirm the structure of absorption bands in the photolysis of thin crystal sheets and emulsion layers ascribed to silver centers by Kirillov, therefore throwing some doubt on the hypothesis of Chibisov.

Frieser and Ranz (213a and b), when experimenting with a radioactive thiosulfate in which the outer sulfur was labeled ^{35}S, showed that $Na_2S_2O_3$ becomes adsorbed to the grain. In the beginning of the ripening, thiosulfate ions could be desorbed by bromide ions when bathing in KBr solution, but not after a certain ripening time. From this, they concluded that first thiosulfate and then Ag_2S become attached to the grain during the ripening. Similar experiments were conducted by Spracklen (214) who concluded that silver sulfide is formed as molecules and sensitization is a process of rearrangement of an inactive form to an active form of silver sulfide.

Harvey ((221) also studied by tracer methods the decomposition of thiosulfate during chemical ripening. He showed that although only a minor fraction of the sensitizer has decomposed at optimum sensitivity, a greater quantity has to be used for highest sensitivity.

In summary, it can be postulated that the end product of sulfur sensitization is Ag_2S, that it is intimately connected with the silver halide crystal, and performs such functions as to provide deeper electron traps than silver, to capture positive holes, i.e., react with halogen and stabilize the silver nuclei on the crystal surface. A still better understanding of the mechanism of these functions and their interrelation is desirable.

b) *Reduction Sensitization*

Photographic gelatins can also contain reducing substances, e.g., sulfite, aldehydes, sugars. Methods for the estimation of sulfite and other reducing substances in photographic gelatin were worked out by Wood (176). A method to determine the amounts of aldehyde was proposed by Armes (204).

The term reduction sensitization was introduced by Lowe, Jones and Roberts (5). They established the difference between reduction sensitization and sulfur sensitization by comparing an emulsion heated with stannous salt with an emuslion heated with a sulfur sensitizer. Earlier, Carroll and Hubbard (38) had pointed to sodium sulfite as an essentiel reducing agent for sensitizing silver bromide. As early as 1927, on the basis of oxidation experiments, Clark (125) concluded that the unexposed silver halide grains contained besides silver sulfide also silver.

In 1959, Chibisov (118) stated that the formation of photographic sensitivity is directly connected with the accumulation of silver centers.

Wood (127, 128) carried out experiments in which he studied pure reduction sensitization by excluding sulfur sensitization. He called it "silver digestion." He used inert gelatin and he afterripened, e.g., at a pH of 7.2 and a pAg of 3.0. The photographic results compared favourably with those obtained when using $Na_2S_2O_3$ as a sulfur sensitizer.

A possible mechanism of the reduction sensitization was offered by Wood: Silver ions are adsorbed on the grain surface in the presence of co-adsorbed OH-ions and are reduced to silver atoms by traces of reducing substances still present even in inert gelatins.

In connection with Wood's publication, it is interesting that Bourne and Loening (129) have analytically shown that hydroxyl ions are adsorbed to a silver bromide precipitate, the degree of adsorption increasing with increasing pH.

Mitchell (112, 66) refers to Wood's paper and explains the reduction sensitization as follows: Small groups of silver atoms are produced which are sheathed in gelatin and not actually in contact with the surface of silver halide. Their function appears to be that of preventing regression of the surface latent image by reacting with liberated halogen.

The basic mechanism of reduction sensitization appears to be the formation of silver atoms by a reaction in which silver ions of the silver halide lattice are reduced. Reduction sensitization is more efficient in the presence of sulfur sensitization. This is explainable, according to Mitchell (36), on the basis that an existing monolayer of silver sulfide on the surface of the silver halide crystal adsorbs silver atoms; or according to Chibisov (206) who emphasizes the catalytic effect of silver sulfide on reduction sensitization. In either case, one can speak of a synergistic effect of reduction and sulfur sensitization.

c) *Gold Sensitization*

The mechanism of gold sensitization as suggested by Mueller (130a and b) and by Koslowsky (6), the original discoverer of the effect, is as follows: In the presence of reducing substances, metallic gold is formed during the ripening and desposited at certain selective sites on the crystal. Since gold is usually added as a complex salt, e. g., thiocyanate or thiosulfate, the complexing agent can etch the crystal surface, thus creating new active sites for the deposition of atomic gold.

A more complicated mechanism was proposed by Mueller (131) later, according to which aurous gold acts as a positive hole trap, pointing to the assumption that metallic gold enters the latent image. This is indicated by the fact that gold sensitized emulsions are only slightly affected by gold latensification (see page 365). Furthermore, it has been shown that the latent image centers in gold sensitized emulsions have greater resistance to oxidation (132, 133).

Spracklen (11) found in gold sensitized emulsions some resistance of the latent image to bleaching by mercuric chloride. Only part of the latent image could be bleached, and the proportion of resistant image increased with extended exposure time. No such resistance exists in gold-free sulfur sensitized emulsions. It was therefore concluded that this resistance of the latent image to bleaching is due to the presence in it of a definite quantity of gold. This gold is formed during the actual exposure and is derived from the surface of the grain of a gold-sensitized emulsion where it is firmly held, possibly in ionic form. Previously, experimental evidence that gold atoms or aggregates of gold atoms are formed during the gold sensitization was presented by Mitchell (66), by Faelens (136a–d) and by Eggert and Fischer (137).

James (218) «gold plated» latent image specks by bathing exposed photographic film in an aurous gold solution, indicating a similar reaction during the gold sensitization.

The similarity in the chemical composition of the latent image centers in gold sensitized (aurous compounds applied during ripening) and gold latensified (aurous compounds applied after exposure) emulsion may point to a similar mechanism. The increased sensitivity of a gold-sensitized emulsion may be due to an increase in size of the sensitivity specks or more likely to a stabilization of the latent image speck, AgAu being more stable than Ag_2. No clarity exists on the question whether in this mechanism gold atoms are added to existing silver or whether part of the silver is replaced by gold, but this question was definitely raised by HAMM and COMER (134). It is also possible that greater catalytic activity of silver-gold or gold centers plays an important part in the mechanism of gold sensitization. While the complete elucidation of the mechanism of gold sensitization has not been accomplished yet, a great amount of knowledge has been collected in the last 33 years of gold sensitization (135).

d) *Combination of Sulfur- and Reduction-Sensitization*

Before gold sensitization was introduced, photographic emulsions were prepared in photographic gelatins containing "natural" sulfur compounds and reducing substances. Silver halide crystals formed and ripened in intimate contact with these chemical ripeners were thus exposed to combined sulfur- and reduction-sensitization.

After the pioneering work by SHEPPARD (3), CARROLL and HUBBARD (4), and STEIGMANN (140), the mechanism of this combined sensitization was studied by HAUTOT and SAUVENIER (109a, 132), POURADIER (138), WOOD (139) and MITCHELL (66).

There is generally agreement that sulfur- and reduction sensitization can be additive. This mechanism involves in its simplest form the formation of silver and silver sulfide centers. HAUTOT (93g) drew conclusions on the nature of these centers from the behaviour of the respective latent image centers during oxidation. He found the latent image centers of the mixed sensitized (sulfur-reduction) emulsions slightly more dispersable (oxidizable) than the latent image centers of a sulfur sensitized emulsion. He concluded that in the case of mixed sensitization, silver sulfide complexes are formed which contain more silver than in the case of sulfur sensitization. Therefore, less photolytic silver needs to be deposited during exposure of a mixed sensitized emulsion, or, in other words, a mixed sulfur-reduction-sensitized emuslion is more sensitive than a sulfur sensitized emulsion.

e) *Combination of Sulfur, Reduction and Gold Sensitization*

Gold sensitization in the presence of reducing agents in gelatin, such as reductones and aldehydes (150) can yield metallic gold. The interaction of gold salts with sulfur compounds in gelatin or with artificially added sulfur sensitizers gives rise to the formation of gold sulfide which had been previously proposed by STEIGMANN (147) and CLARK and MITCHELL (9).

STEIGMANN (40) first pointed to a possible complexing of gold with gelatin. This was later quantitatively proven by KRUMMENERL (148) and NARATH and TIILIKKA (41).

TAVERNIER and FAELENS (136d) could even show that in the presence of gelatin, 95% of the gold applied as aurous dithiocyanate is not available for sensitization because of the formation of a more stable "gold gelatinate." Certain modifications of gold sensitization in the presence of gelatin can be expected from microcomponents in the gelatin, such as active sulfur compounds, reducing substances and restrainers.

HAUTOT and his school (93b, c, 132) made considerable contributions towards the unraveling of the mechanism of the combined sulfur, reduction, and gold sensitization with the help of oxidation studies. Before chemical sensitization, the centers of chemical sensitivity are the internal and external crystal defects. The sensitization with reducing agents will lead to centers consisting of metallic silver, and the sensitization with labile sulfur compounds will yield silver sulfide.

These assumptions were supported by oxidation experiments. Treatment with a solution of diluted chromic acid (0.25%) had no influence on the primitive sensitivity (no chemical sensitization applied) of a photographic emulsion. But the speed increase obtained with sulfur and reduction sensitization could be diminished with this chromic acid solution.

Before gold sensitization was introduced, it was known that the external latent image of an emulsion prepared with an inert or active gelatin was oxidizable with dilute chromic acid solution. HAUTOT and co-workers found that the latent image of sulfur- and reduction-sensitized emulsion could be bleached but that gold-sensitized emulsion possessed an external latent image which was more resistant to oxidation. Only with a very dilute solution of chromic acid (0.025%) could a noticeable difference be observed between the latent image of a sulfur- and reduction-sensitized emulsion, the sulfur-sensitized emulsion yielding the more stable latent image. The latent image of a combined gold- and sulfur-sensitized emulsion is most resistant to oxidation.

An extensive study of the mechanism of gold sensitization in the presence of thiosulfate by FAELENS and collaborators (50, 136c, 149) led to the conclusion that sodium thiosulfate in the presence of aurous dithiocyanate will not act as a sulfur sensitizer. It will rather remove gold from the gold-gelatin complex and make it available for sensitization. In this mechanism, silver aurous dithiosulfate is formed on the silver halide crystal surface, where it will decompose during ripening into silver-gold-sulfide. It may also remain partially intact and become functional during the latent image formation, which is in agreement with the findings of other authors (11, 93, 132, 133, 134).

More precise information on the mechanism of gold-sulfur sensitization could be obtained by Faelens and co-workers (51 a and b) in a gelatin-free, pure silver bromide suspension. As sensitizing agent, they used gold thiosulfate [$Na_3(AuS_2O_3)_2$].

Two entirely different techniques were used. In a potentiometric titration, the addition of sodium aurous dithiosulfate showed an immediate decrease of *p*H. This was explained by a decomposition of the adsorbed complex according to the following equation:

$$5\,AgBr + 3\,Au(S_2O_3)_2^{3-} + 2\,H_2O \rightarrow AgAu_3S_2 + 4\,AgS_2O_3^- + 2\,H_2SO_4 + 5\,Br^-$$

Continued ripening led to the formation of the final product of this type of sensitization, silver-gold-sulfide, AgAuS, as follows:

$$AgAu_3S_2 + AgS_2O_3^- + AgBr + H_2O \rightarrow 3\,AgAuS + Br^- + H_2SO_4$$

These reactions were further proved by a second method in which the ripening was conducted with radioactive sodium aurous dithiosulfate with labeled gold ^{198}Au and with inner and outer labeled sulfur ^{35}S. From activity measurements on these so sensitized silver bromide suspensions, Faelens and co-workers could draw the interesting conclusions that, at maximum sensitivity, aurous ions are completely built into the silver bromide lattice and that, at the same time, sulfide ions are formed. The correctness of the chemical equations derived from the first technique was also proven.

Although the results by Faelens and co-workers appear very convincing, the conclusions which were reached earlier by Mitchell (44) on mixed sensitization (silver, gold, sulfur) deserve consideration. On the basis of his experiments with single silver bromide crystals, Mitchell indicates that one prerequisite is the existence of strained crystals or crystals with imperfect surfaces, on which the products of chemical sensitization, silver, gold or silver sulfide are deposited in a state of extremely fine dispersity. The silver sulfide forms a monolayer on the surfaces of the strained regions of the crystals while silver and gold exist as small groups of atoms at the interface of crystal and gelatin. Since silver and silver sulfide have a strong affinity for each other, the silver will be concentrated where the Ag_2S is. Then the gold will replace the silver.

Considering the results of all these investigations on the mechanism of the combined sulfur, reduction and gold sensitization, the following conclusions can be drawn:

1. The sensitivity specks obtained by using active gelatins resemble those obtained when artificially applying a sulfur sensitizer, such as $Na_2S_2O_3$. They could consist of silver sulfide on which metallic silver is adsorbed, attached or concentrated.
2. The sensitivity specks obtained with a reduction sensitizer such as stannous chloride, as well as the corresponding latent image, appear to be chemically identical and consist most likely of metallic silver.
3. The sensitivity specks and the latent image of a gold-sensitized emulsion, which resist oxidation, appear to be chemically different from those obtained by sulfur or reduction sensitization and were believed to consist of silver and gold until Mitchell and also Faelens could shown that it is more plausible that they consist of at least, in part, of gold-sulfide or of silver-gold-sulfide, AgAuS.

The "gold effect" may be based on more than one mechanism. Gold atoms may be superior to silver in catalyzing development. Gold-sulfide or silver-gold-sulfide formed during chemical ripening may act as positive hole acceptors and gold ions which have entered the silver halide crystal may serve as effective electron traps. Also, AgAu or AgAuS may be more stable than Ag_2 (sub-latent image) or Ag_2S, respectively.

f) *The Nature of Fog Centers*

Regardless of the type of sensitization applied, upon prolonging the afterripening or increasing the concentration of the chemical sensitizers, a state is finally reached where developable centers are formed without the need of exposure to light. This state is known under the term of "fog." A better knowledge of the nature of the fog centers should be helpful in the understanding of the mechanism of chemical sensitization, if one could assume that they are chemically identical with the sensitivity specks.

The fog which commonly occurs when photographic gelatin silver halide emulsions are ripened beyond the point of maximum sensitivity was studied by Chibisov and Titov (151). They concluded that the fog nuclei are silver particles which have reached a certain critical size.

Chibisov and co-workers (152, 153) also pointed to the amorphous structure of the fog centers resembling in this respect the latent image centers, which, due to their small size (only a few silver atoms at the minimum), are also assumed to be amorphous.

A systematic study of fog centers in reduction, sulfur and gold sensitizing was described by Hautot (93 b).

Fog centers of reduction-sensitized emulsion, like the latent image, proved to consist of more metallic silver than the sensitivity specks. They become easily oxidized. By applying chromic acid solutions of different concentrations, and surface and internal developer, respectively, it was even possible to distinguish between the internal and external fog centers, a more concentrated oxidizer being required to destroy the internal centers.

Fog centers of sulfur-sensitized emulsions consist of silver and silver sulfide. They behave differently from those of reduction sensitized emulsions in that they are less easily oxidized.

The nature of these fog centers was also studied by BASSETT and DICKINSON (141) by sensitizing emulsions with different amounts of thiourea and subjecting them to a bleach of chromic acid and also to a treatment in dilute solutions of gold thiocyanate prior to exposure and development. These investigations support the view that fog centers can consist of silver and silver sulfide.

Fog centers of gold-sensitized emulsions behave as if they contain gold. They very strongly resist the attack of oxidizing agents.

Fog centers of gold-sulfur combination sensitization are believed to consist of gold sulfide and silver.

Fog centers of reduction-gold combination sensitization behave like gold-silver particles containing more gold and silver than the sensitivity specks.

F. *Other Methods of Sensitization*

a) *Sensitization with Noble Metals from the Platinum Group*

The difference in efficiency when sensitizing with platinum and palladium salts in gelatin-free suspensions and in the presence of gelatin was already discussed (see paragraph C-c, page 356). The patent literature (226a) discloses the enhancing of sensitivity of photographic silver halide emulsion by the incorporation of water-soluble salts of platinum metals in group VIII of the periodic system and (226b) the effect of palladium salts to sensitize the emulsions sensitized with gold compounds and to reduce the reciprocity failure at low intensities.

Sensitization studies with ammonium chloroiridite were carried out by MITCHELL and collaborators (9, 44), STEIGMANN (154) and WEST and SAUNDERS (67). WEST and SAUNDERS found the sensitizing effects of ammonium chloroiridite, $(NH_4)_3 IrCl_6$, and ammonium chloroiridate, $(NH_4)_2IrCl_6$, identical. Both salts enter a reversible redox equilibrium, and silver chloroiridate spontaneously decomposes to form silver chloroiridite (155).

The contrast-improving properties (i.e., steepening of gradation)—(see curve in reference 29f)—of rhodium salts were described by POKORNY (158), and a mechanism proposed by WELZEL (159), according to which a selective destruction of sensitivity centers, most likely in the larger grains, takes place.

b) *Sensitization by Other Metals and Compounds*

LARSON, MUELLER and HOERLIN (131, 160) reported that bivalent lead or cadmium ions, when co-precipitated with silver halide to increase the sensitivity of iodobromide emulsions to X-ray and gamma radiation, simultaneously decrease the sensitivity to light.

BERRY and SKILLMAN (227) attributed the effects of lead ions to their adsorption on the silver bromide surface and emphasized the reduction of rate of OSTWALD ripening.

POLSTER (156) reported the increase of sensitivity of an emulsion to X-rays by thallium ions and the co-precipitation of these ions were investigated by HIRSCH (157).

Many compounds have been proposed in the patent literature as "sensitizers" in photographic emulsion, e.g., polyoxyethylenes (162), but most of these are considered to function as development accelerators (29b and 224).

c) *Hypersensitization*

Hypersensitization is a method to increase the sensitivity of a photographic emulsion before exposure. The sensitivity increase can be accomplished by bathing film in pure water, whereby presumably bromine ions are removed and the silver ion concentration is increased (179, 180). Other methods comprise bathing in various solutions such as ammonia, amines and silver salts (181, 182). Hypersensitization of nuclear emulsion (used to record the photographic effect of ionizing particles such as α-particles, electrons, protons) with triethanol amine has been described in the literature (183, 184) and the effect ascribed to the generation of centers for capturing electrons in the conductivity band. The same explanation can apply in the hypersensitizing by short pre-exposure.

Hypersensitization has been reported to decrease the low intensity reciprocity law failure (185, 186) which is of particular interest in astronomy and spectrography where usually long exposures are required due to the low light intensity available.

Mercury vapor hypersensitization, proposed by DERSCH and DUERR (126), also considered an example of reduction sensitization (5, 187), may be attributed to the formation of an amalgam with silver specks. The same mechanism may apply to the latensification (see next paragraph) with mercury (126), however, with the difference that the amalgam is formed with the latent image.

d) *Latensification*

Whereas hypersensitization effects some of the products of chemical sensitization, e.g., silver specks, latensification is believed to modify the latent image. The term latensification is used for those methods which are applied after exposure for the purpose of increasing the sensitivity of a photographic emulsion. This sensitivity increase can be accomplished with certain chemical solutions or vapors or with an overall low intensity post-exposure (200).

Latensification by mercury vapor is more stable than the corresponding hypersensitizing effect and does not change the shape of the reciprocity curve (29c). This effect and also the latensification by low intensity post-exposure can be explained as follows (Sheberstov and Vendrovskii, 194): The size of the latent image centers are increased, resulting in an increase in the rate of development.

Chemical agents which produce latensification were described by Sheppard, Vanselow and Quirk (188). Latensification with aurous thiocyanate or thiosulfate was described by James, Vanselow and Quirk (76) and by Mueller (130a).

Latensification can be achieved with hydrogen peroxide (189), with organic peroxides, such as benzoyl peroxide (191a and b, 192, 193), and with perborate (190). Other effective latensifying agents are sulfur dioxide (195), bisulfite (196) and vapors of organic acids, such as formic acid or acetic acid (197), guanidine carbonate (198), polyalkylene amines (199).

The mechanism of latensification can be explained as an increase in size of sub-image centers (centers which do not contain enough silver atoms to make them developable), or as an increase of the number of mobile silver ions (188), or more precisely, as a release of surface silver ions leading to a reduction to silver at the sub-image and latent image centers.

III. Summary, Conclusions and Outlook

The theroretical considerations involving the chemical sensitization and the formation of the latent image are still, in part, highly speculative. The application of solid state physics and chemistry has considerably aided in getting a clearer understanding of these relationships. It is expected that more work in this theoretical field will eventually lead to an elucidation of the mechanism of chemical sensitization.

Great difficulties still exist in the correct interpretation of the combined (gold, sulfur, reduction) sensitization. The conception of the Russian scientists, under the leadership of Chibisov (206) has been very stimulating. A better understanding of the correlation of the different types of sensitizations has been accomplished by Hautot and his school (93). Recent contributions by Faelens (51a und b) seem to point the way to the elucidation of the mechanism of the combined sensitization.

With a deeper understanding of these mechanisms, it may be possible to answer the question about the ultimate sensitivity of the photographic silver halide emulsion. A special conference on "The Ultimate Sensitivity in Photography" was held by the Royal Photographic Society in London in December 1960 (207), and these are some of the principal conclusions: One pre-requisite for obtaining ultimate speed is the best possible quantum yield of the photographic emulsion. Farnell and Chanter (209) pointed out that grains of high speed photographic emulsions have to absorb four quanta in order to make them developable and that the minimum size of a developable latent image speck consists of four silver atoms. Confirming this, Klein (210) drew the conclusion that the sensitivity of the most sensitive grains known today could only be increased by a factor of 4, even if it were possible to render grains developable by absorption of only one quantum. Similar conclusions were reached by Vendrovskii and Sheberstov (211). Frieser (212) pointed out that the photographic process cannot be improved beyond certain limits for practical and theoretical reasons, limiting factors being, for instance, graininess.

In conclusion, it must be admitted that it is difficult to reconcile all the various ideas about the possible mechanism of chemical sensitization. One is reminded of many doors, for each of which one needs a different key. There is no master key available yet to open all the doors. In 1951, Professor Berg (219a and b) gave a very fine review on the mechanism of chemical sensitization in Birmingham (England). At that time, Dr. Berg stated that "it is difficult to find one's way through the labyrinth of facts which have become known on chemical sensitization." Even today, we have not yet found our way out of this labyrinth.

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