# One-Photon Mechanism for Silver Halide Imaging: Implications and Implementation

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Silver halide photography has the potential for the ultimate photographic efficiency - the one-photon process - coupled with amplification. A practical non-fogging one-photon mechanism for the silver halide photographic process, long considered unachievable, was developed and experimentally supported.[1] Consequences of this process for the design of photographic products, and implication for practical applications will be discussed. Directions for the experimental implementation of this process will be suggested.

The one-photon process for latent image formation is summarized in equation (1):

$$h\nu + Ag_2(E) + Ag_2(H) \text{ ----> } Ag_4 \qquad (1)$$

Here, hν is the photon energy, $Ag_2(E)$ is an electron trapping center, $Ag_2(H)$ is a hole-trapping center that acts by the Lowe mechanism, and $Ag_4$ is a latent image center.[1] The concept was experimentally supported for hydrogen sensitized silver halide systems.[2] This process depends on the simultaneous formation of mobile photo holes and photoelectrons and is not triggered by thermal processes.

The efficiency of the one photon process relative to a four-photon process is demonstrated in Figure 1.

For a given photon density, as indicated by the arrows, the photographic sensitivity of the four-photon process is limited to crystal sizes that will absorb at least four photons during the exposure. Photographic sensitivity of the four-photon process is further reduced by inefficiencies due to electron-hole recombination and less than maximum quantum efficiency of the photoelectron in each latent image forming step.[1] Overall, the relatively large crystal sizes required for practical photographic systems is the result of their relatively low quantum efficiency. The same restrictions apply to the sensors in electronic imaging chips.

In contrast, light absorption has no restrictions on the crystal size for the one-photon process. As indicated in Figure 1, the smallest crystal with one-photon efficiency will respond to photon exposure. Thus, the crystal size is no longer a critical factor necessary to control light absorption. Instead, the crystal size can be adjusted to provide the amplification necessary to provide sufficient image density after development.

The one-photon sensitivity has technological consequences for film building:

- Super-fine grain images
- Silver savings
- Thinner film layers
- Smaller silver halide crystals
- Increased sharpness
- Reduced coupler lay-down
- Reduced image controlling chemistry in the film
- Higher processing rates
- Improved processing ecology

Additional advantages can be envisioned.

The energy requirements for the one-photon process were estimated from spectral sensitization studies of reduction sensitized emulsions. Using the redox-potential of the dyes to determine the effective energy thresholds

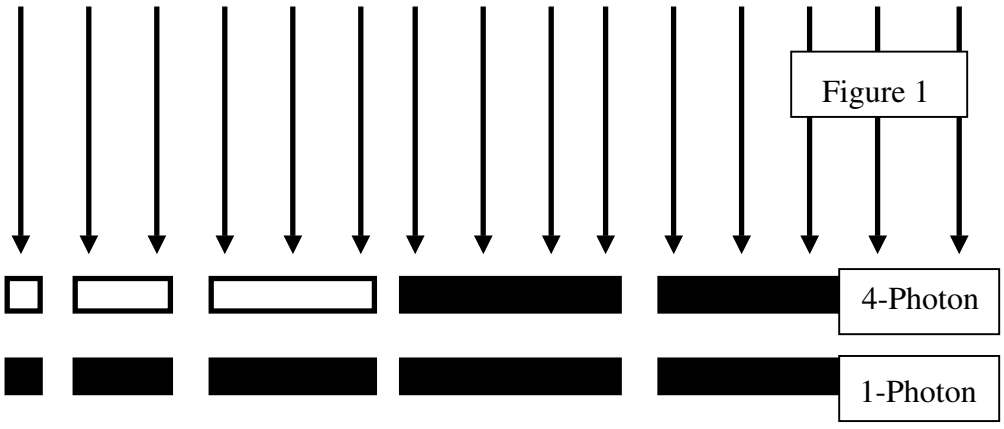


Figure 1

for spectral sensitization the threshold for the photon electron processes was determined to about –1.0 (V vs. Ag/AgCl).[3]

For the one-photon mechanism, photo holes must be provided with energy that can provide the Lowe-mechanism of oxidizing $Ag_2$ (H) centers. In the redox energy scheme, these dyes must have an oxidation potential more positive than +0.4V.[3]

The minimum energy requirement is the (absolute) sum of these two energy levels, about 1.4 eV. This energy can not be provided by thermal electrons (about 0.03eV) but must be provided by absorption of photons. Sensitizing dyes used in practical photographic systems generally have reduction potentials more negative than –1.0V, and oxidation potentials greater than 0.4V. Thus, effective spectral sensitization of the one-photon process is anticipated for practical systems. The longest spectral sensitization for J-aggregating dyes absorbed to AgBrI can be estimated to about 740nm. This is well within the range of red sensitization of color films (< 700nm).[3]

The experimental formation of hole-trapping $Ag_2$(H) centers is well established, for instance, using stannous chloride, high pH treatment, or aminoboranes. This information is available from the general literature.[4] For the experimental discovery of the one-photon process, hydrogen sensitization was used, which apparently provided both electron and hole trapping $Ag_2$ centers.[2]

The formation of electron trapping $Ag_2$(E)centers is implied in the hydrogen sensitization that experimentally led to the one-photon process. Non-developable electron trapping $Ag_2$(E) sub-latent images are formed by low exposure of silver halide systems. Thus, low-intensity pre-exposure may be an experimental procedure to develop reduction sensitization processes that lead to non-developable electron trapping $Ag_2$ centers.

The formation of both hole trapping and electron trapping $Ag_2$ centers on the same crystal needs to be achieved without their interaction before exposure and without fog formation. The experiment implies that they form at different places on the crystal. Electron trapping $Ag_2$ centers can be stabilized by forming on positively charged sites, while hole trapping $Ag_2$ centers will be activated by forming on crystal centers that provide negative charges. Their interaction can be provided by appropriate photo-neutral adsorbents to the silver halide surface. Sensitization controlling addenda are regularly used in chemical and spectral sensitization. Examples are sodium thiocyanide NaSCN and tetra-aza-imidazoles and derivatives.[4]

Another aspect of optimizing the photographic process is the prevention of electron – hole recombination after exposure. Hole-trapping reduction sensitization required for the one-photon process reduces the number of mobile holes and thus contributes to the decrease of electron – hole recombination.

Electron-hole recombination can also be reduced by temporary electron trapping. This is exemplified by the effect of controlled iridium doping.[5] Iridium, when present in the crystal at low concentration, will temporarily trap electrons, and release the electron for latent image formation. This allows the photo hole to react with a hole-trapping $Ag_2$(H) center to form secondary electrons which react with electron trapping $Ag_2$(E) centers and interstitial silver ions to form metastable $Ag_3$ centers. These are stabilized by interstitial silver ions to form $Ag_4^+$, and the electrons released from the iridium centers to form $Ag_4$ latent image centers. The degree of electron trapping by iridium centers can be controlled by dopant concentration[5] and by the depth of incorporation in the crystal.[6]

In conclusion, the one-photon process for latent image formation in silver halides provides significant technical advantages for the improvement of high speed films and fine grain papers. The sensitization technology to impart one-photon sensitivity has been shown to be known, and the development to film and paper products appears straightforward. Considering that it has been reported that a two hundred speed 35 mm color negative has the capacity of recording two hundred mega pixels of information,[7] the one-photon process will allow to multiply this imaging capacity. Thus, the one-photon process for silver halide imaging systems allows to significantly strengthen the superiority of silver halide photographic systems over competing imaging systems.[8]

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