11.4 Silver Photography

Silver Halides

Silver halides, AgX, are wide-bandgap semiconductors, with $\Delta E_g = 2.4 - 3.0$ eV. Silver chloride is colorless, silver bromide pale yellow and iodide yellow. Silver halides are effective ion-conductors due to Frenkel disorder, yielding interstitial cations $\text{Ag}^+_i$ and vacancies $V_{\text{Ag}}^-$ on the sites normally occupied by $\text{Ag}^+$ cations:

$$ \text{Ag}^+_L \rightleftharpoons \text{Ag}^+_i + V_{\text{Ag}}^- $$

Both types of defects ($\text{Ag}^+_i$ and $V_{\text{Ag}}^-$) are rather mobile at room temperature. Mass transport through $\text{Ag}^+$ cations diffusion is thus possible within the silver halide lattice.
Formation of the latent image

Ag$^+_i$ defects represent efficient traps for conduction band electrons. V$_{Ag^-}$ vacancies tend also to trap valence band holes.

Under bandgap irradiation, photogenerated electrons and holes are therefore readily trapped and eventually produce the photo-corrosion of the material:

$$\text{AgX} \quad \text{hv} \quad e^- + h^+ (\text{AgX}) \quad \text{Ag}^0 + \frac{1}{2} X_2$$

The actual photochemical process of the silver halide photography consists in the formation of Ag$^0$ clusters in the AgX-crystal during exposure to light. These silver clusters constitute the latent image. The efficiency of the charge separation process determines the quantum efficiency of the photographic material and can be optimized by employing layers of different halides compositions.

Silver is a noble metal: $E^0(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V vs SHE}$, so a high stability of the latent image towards oxidation by O$_2$ is ensured.
**Chemical processing (image development)**

The photographic development is a selective reduction of silver halide to metallic silver, which is catalyzed by Ag$^0$ clusters constituting the latent image. The developed image is made of reduced metal silver grains. Areas exposed to light appear black after development, while unexposed areas remain white. The resulting image is thus **negative**.

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**Exposure**

- Irradiation of AgX grains
- Latent image = surface Ag$^0$ clusters

**Development**

- Chemical reduction of Ag$^+$ catalyzed by Ag$^0$ clusters (image amplification)
- Undesired partial reduction of unexposed silver halide grains

**Fixing**

- Image fixing by dissolution of remaining AgX
Chemical processing (image development)

Developers are mild reducing agents, a few examples of which are provided here below. Driving force for the reduction of $\text{Ag}^+$ is kept as small as possible, as to ensure selective reduction of irradiated silver halide grains. Since the redox potential of the developers decreases with growing pH value, the development process is often only possible in aqueous alkaline solution above a certain pH value.

In color films, special p-phenylene-diamine derivatives are used as developers that are designed to allow for a rapid reaction with color-forming couplers.
AgX grain morphology and photographic sensitivity

AgX crystals (mostly AgBr) are precipitated during the jet mixing of AgNO₃ and alkali halide in an aqueous gelatine solution at elevated temperature. The resulting dispersion is called photographic 'emulsion'. The shape and size distribution of AgX grains can be varied by changing the experimental conditions.

The size of AgX grains determines the chemical amplification factor during the image development. The larger the grains the larger the amplification factor and the more sensitive the photographic film.

Large grains, however, obviously decrease the spatial resolution of the picture and imply an increased thickness of the photographic emulsion.
Spectral sensitization

The intrinsic sensitivity of silver halide (essentially AgBr) comprises only the UV and blue range of the visible spectrum. By means of dye-sensitization (Vogel, 1873), the sensitivity range can be extended as far as to $\lambda = 1.2$ μm.

Compounds with a polymethine structure, especially cyanine dyes and merocyanine dyes are suitable spectral sensitizers. These compounds are tightly adsorbed on the AgX surface, mostly in the form of H- and J-aggregates.

A panchromatic film is a type of black-and-white photographic film that is sensitive to all wavelengths of visible light, thanks to a mixture of several dye-sensitizers. By varying the concentration and/or efficiency of each sensitizer, a panchromatic film produces a realistic image, in which colors are translated into different grey shades.
**Black-and-white photographic films and papers**

### Negative film
- Overcoat
- Emulsion 15 µm
- Antihalo undercoat
- Dyed film base 140 µm
- Conductive layer

### Photo paper
- Overcoat
- Emulsion 3-5 µm
- PE with TiO<sub>2</sub> pigments
- Paper 160 µm
- PE film 30 µm

### X-ray film
- Overcoat
- Emulsion ~15 µm
- Blue-dyed base 180 µm
- Emulsion ~15 µm
- Overcoat

### Material Table

<table>
<thead>
<tr>
<th>Material</th>
<th>AgX</th>
<th>Grain diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative film</td>
<td>AgBrI</td>
<td>0.7 µm</td>
</tr>
<tr>
<td>Photo paper</td>
<td>AgClBr</td>
<td>0.3 µm</td>
</tr>
<tr>
<td>Microfilm</td>
<td>AgClBr</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>X-ray film</td>
<td>AgClI</td>
<td>1.5 µm</td>
</tr>
</tbody>
</table>
**Color vision**

There are two different types of photoreceptors in our retina: cones and rods. Rods are sensitive to very low light intensities. They are relatively slow to respond to changes and are used mainly for night- and peripheral vision. Light picked up by the rods is treated by our vision as monochrome.

Cones are less sensitive to light, but react faster to changes in intensity. They are concentrated in the central part of the retina (fovea). Cones are divided into three types. S cones are sensitive to blue light and M cones to the yellow and green spectral domains. L cones are sensitive to red light and, in a lesser extend, also to the blue. Human vision is thus essentially trichromatic.

While "color-blind" people usually miss one of the three cone types, studies suggest that some humans (up to 50% of women and 8% of men) actually possess four types of cones (tetrachromacy).
Three-colors mixing principle

The three-color mixing method, which is the foundation of virtually all practical color processes, whether chemical or electronic, was first suggested in 1855 by Scottish physicist James Maxwell. Maxwell found that all the colors of nature could be reproduced by mixing only three pure colors of light – red, green and blue – in proportions which would stimulate the three types of human retina cones to the same degrees that the "real" colors.

In most color prints, the primary dye colors used are cyan, magenta, and yellow. Cyan is the complement of red. Magenta is the complement of green, and yellow the complement of blue. Combinations of different amounts of the three inks can produce a wide range of colors.
Additive and subtractive color mixing

The first permanent color photograph was taken in 1861 using Maxwell's three-color-separation principle: Three separate black-and-white photographs through red, green and blue filters were taken. This provided three basic channels required to recreate a color image. Transparent prints of the images could be projected through similar color filters and superimposed on the projection screen, an additive method of color reproduction. A color print on paper could be produced by superimposing prints of the three images made in their complementary colors, a subtractive method of color reproduction pioneered by Louis Ducos du Hauron in the late 1860s.

A photograph of the Emir of Bukhara, taken in 1911 using three exposures with red, green, and blue filters.
**Color reproduction by color forming method**

This technique (Agfa, 1936) is the basis of the most successful color-photographic materials. Color formation takes place in the course of the development on the exposed AgX grains by the reaction of a developer oxidation product with color forming agents.

![Diagram of color reproduction process]

Depending on the chemical structure of the coupler present in the three respective emulsion layers, yellow, magenta and cyan image dyes are obtained.

The types of dyes that can be obtained by such a simple coupling reaction is rather limited, and obtained image dyes are not very stable under day light.
Photographic color systems

\[
\begin{align*}
\text{NH}_2 & \quad R_1 \\
\text{R}_2 & \quad \text{R}_3 \\
\text{N} & \quad \text{N} + 2\text{Ag}^+ + \text{OH}^- & \quad \text{NH} & \quad \text{R}_1 \\
\text{R}_2 & \quad \text{R}_3 \\
\text{N}^+ & \quad \text{N}^+ + 2\text{Ag}_0 + \text{H}_2\text{O}
\end{align*}
\]

Color developer

\[
\begin{align*}
\text{NH} & \quad \text{R}_1 \\
\text{N}^+ & \quad \text{R}_2 \quad \text{R}_3 \\
\text{N} & \quad \text{N}_A \quad \text{C} \quad \text{B} \\
\text{R}_2 & \quad \text{R}_3 \\
\text{N}^+ & \quad \text{C} \quad \text{A} + \text{HX}
\end{align*}
\]

Dye coupling

coupler
dye

Color couplers:

yellow
magenta
cyan
Positive-negative process

The preferred way to a colored positive image consists of two stages:
For the recording, a color negative film is used, which gives a color negative after color development and fixing. After printing on color print paper, a positive picture is obtained.
Because films have to be rolled in a camera, the thickness of each of the emulsion layers is limited to \(~3-5\ \mu m\). This also impose a limit to the size of the AgX grains.
Negative-positive process

White light

Negative

1. layer sensitive to blue light
2. layer sensitive to green light
3. layer sensitive to red light
4. base substrate

Development and in-situ dye synthesis

Positive image

Actual structure of a negative film (Kodak, ISO 1000 / 31° DIN)

- protection layer: 2 µm
- high-sensitive blue: 2.5 µm
- low-sensitive blue: 2.5 µm
- high-sensitive green: 3.2 µm
- high-sensitive red: 2.5 µm
- low-sensitive green: 4.7 µm
- low-sensitive red: 5.6 µm
- anti halo layer: 3.2 µm
- polymer base
- conductive layer
Reversible (diapositive) color film

The obtaining of a positive image in a single-stage way is possible by changing the processing method:

The exposed film is first developed with a black-and-white developer. The developed film is then exposed to uniform white light (solarization).

Black image silver particles block in a large extent the light in this second exposure. Only AgX crystals, which were not exposed in the first place, are thus irradiated during this step.

Final operations comprises conventional processing with a color developer and fixing.

This method allows in particular for the economical production of transparent color slides and movie films copies.
Silver dye bleach process (Cibachrome / Ilfochrome)

This technique (Ciba 1963) is based on the bleaching of azo dyes by image silver:

\[ 4 \text{Ag}^0 + \text{N=N} + 4 \text{HCl} \rightarrow 4 \text{AgCl} + 2 \text{NH}_2 \]

The unexposed material contains a non-diffusing yellow, magenta and cyan azo dye in the blue-, green-, and red-sensitive layer, respectively. After exposure, the material is processed into a positive image by black-and-white development, bleaching in a strongly acidic solution, and fixing. This technique allows to make light-fast color prints from color slides.

Azo dyes present in the material filter the light necessary to the excitation of the sensitizers. The sensitivity of the process is thus quite low and is not convenient for use in a camera film.
**Color image transfer process**

![Diagram of the color image transfer process](image)

Instant color photography (Polaroid, 1963) is based on the immobilisation of oxidized dye developer molecules upon reduction of light-exposed AgX grains.

- **Soluble (mobile)**
  - OH
  - Dye

- **Insoluble (immobile)**
  - OH
  - Dye

2 Ag⁺ → 2 Ag⁰
- 2 H⁺

**Reagent (NaOH)**
- Blue-sensitive AgX layer
- Yellow dye-developer
- Blocking spacer layer
- Green-sensitive AgX layer
- Magenta dye-developer
- Blocking spacer layer
- Red-sensitive AgX layer
- Cyan dye-developer

**Neutralizing (acidic) layer**

**Black plastic base**