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# *Holographic photochemistry, a summary*

MAS 450/854

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## **Introduction**

In holography class, we use “silver halide” plates exclusively as our photosensitive medium. “Silver halide” (sometimes referred to as AgH) is a term that includes silver chloride (AgCl) and, most commonly and also for our plates, silver bromide (AgBr). These plates are coated with an emulsion of gelatin (animal renderings, just like Jello™) in which is suspended grains of silver halide crystals.

These silver halide grains are sensitive to light. When a plate is exposed to light, a photons from the light source stream through the emulsion. Once in a while, a photon bumps into a silver grain. If a certain number of photons hit a grain, a small site of metallic silver is formed on that grain. Think of this site as being a mark on a silver halide grain. The chances of a grain being marked depends on the size (surface area) of the grain, the amount of light, and the length of exposure. In holographic emulsions, the grains are very fine (have a small surface area) in order to reproduce small fringes, so they aren't very likely to be marked and thus such emulsions aren't very sensitive. Collectively, the marked grains form a “latent” image: an invisible yet recorded pattern in the emulsion.

## **Developers**

All of our plate processing begins with development. Developers are responsible for turning marked silver grains completely to metallic silver, which looks black when it is very small. Developers “amplify” the effect of exposure and make photography as we know it possible.

We use several developers during the course of the class. The first, D-19, is a commercially available photographic developer. It is “lower energy” (can only produce lower contrast results) than the other developers we use. In fact, all of the other developers are of such energy that they are mixed and stored in two parts; when mixed together, the different parts quickly consume and exhaust themselves.

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The choice of two-part developer is mostly based on how it affects the thickness of the emulsion layer itself. When a photographic plate is put in a water solution (like developer), it swells up like a sponge. The developer “pyrogallol”, which consists mostly of the developing agent by the same name, hardens the sponge in its swollen state so that it is difficult for it to shrink back down. Because of its action on animal products like photographic gelatin, pyrogallol is called a “tanning” developer.

On the other hand, “PAA”, composed of sodium phosphate dibasic and ascorbic acid, doesn’t harden the emulsion at all. The thickness of the emulsion is free to change. “Ilford” developer is a blend between “pyrogallol” and “PAA”, having both “pyro” and ascorbic acid. It is designed to hold the thickness of the emulsion approximately the same as it was before exposure (when it was still dry). No matter what the developer, the final thickness of the emulsion is also dependent on the action of the bleach (if any).

#### **Stop Bath**

Developers are weak bases. The next step in processing, the “stop bath”, is a weak acid (acetic acid). Stop bath neutralizes the developer and stops the development process.

#### **Fixer**

“Fixer” is a chemical used to remove silver halide from an emulsion, leaving only silver. In other words, the image becomes “fixed” or made permanent. Fixer’s main ingredient is sodium thiosulphate. Conventional black and white photographic processing uses a “develop–stop–fix” sequence to develop silver and then remove all of the unexposed photosensitive material. Holographic processing only uses fixer if the plate is not to be bleached (leaving it an “amplitude grating”), or if the plate is going to be bleached with a “rehalogenating” bleach such as bromine water (see below).

#### **Bleaches**

Bleaches give the modern hologram its efficiency and brightness. A bleach turns an amplitude grating into a “phase grating”, which usually appears clear but actually contains changes in index of refraction that form an efficient grating structure. Bleaches turn the dark areas of the plate clear; the exact method depends on the bleach type. We use the following bleaches during the course of class:

- physical transfer (ferric sodium EDTA or just “EDTA bleach”): Uses an unfixed plate. Makes the exposed silver soluble, converts it to silver halide, and redeposits it in the areas that have silver halide already, thus “physically transferring” material from one part of the emulsion to another. Because little net material is lost in the emulsion, EDTA bleach is used when shrinkage should be kept to a minimum.
- reversal bleaches (potassium dichromate): When an unfixed plate (one containing both silver and unexposed silver halide) is placed in reversal bleach, the silver is made soluble and is taken up into solution (or washed away later), leaving nothing where the silver was and leaving the silver halide undisturbed. Causes emulsion shrinkage.

- rehalogenating bleaches (bromine water): Used with a “fixed” plate (one that contains only silver in the exposed areas, and no unexposed silver halide). Turns the silver back to silver halide. Bromine water is thought to prevent printout by leaving extra bromine in the emulsion that prevents silver halide from turning back to silver when exposed to light over time. Bromine water is a dangerous chemical that should be handled only under the fume hood. Causes the emulsion to shrink.

#### Washing and drying

Washing removes development chemicals and water soluble products from the emulsion. Methanol drying causes the water in the emulsion to gradually be replaced with alcohol, which dries much faster. We use three baths of methanol-water solutions, consisting of 50%, 75%, and 100% methanol.

The color of the alcohol baths is due to sensitizing dyes in the emulsion. Silver halide is not necessarily very sensitive to the wavelengths of light that come from our lasers, so a dye is put in the emulsion that absorbs those frequencies and “re-radiates” them at wavelengths to which the silver halide is sensitive. Some of those dyes are not very soluble in water, but are soluble in the alcohol baths.

#### Miscellaneous

TEA (Triethylamine) is used to swell the emulsion of a reflection hologram before exposure. TEA is an oily, thick liquid, mixed in small parts (0 to about 10 percent) with equal amounts of isopropanol and water. It washes out in the developer or in a water prewash. TEA increases the sensitivity of the plate: use about two-thirds of your normal exposure when using it.

#### Common processing techniques

✓ D-19 developer ⇔ stop bath ⇔ fixer

Closest to conventional photographic processing. Limited contrast. Amplitude holograms.

✓ Ilford developer ⇔ stop bath ⇔ EDTA bleach

Limits shrinkage of the emulsion, used for masters, transmission transfers, and “red” reflection holograms (or when using TEA to preswell).

✓ Pyrogallol ⇔ stop ⇔ potassium dichromate bleach (“Pyrochrome” process)

✓ Ilford ⇔ stop ⇔ potassium dichromate

Sometimes used for reflection holograms. Bleach causes some shrinkage, producing orange holograms. The eye is not very sensitive to “Helium-Neon red”, so orange holograms appear brighter.

✓ PAA ⇔ stop ⇔ fix ⇔ bromine water

Used for transmission transfers to maximize brightness and to preserve the final plate from print-out. Causes shrinkage that changes the “tip angle” of the hologram; compensate by using a different (slightly steeper) reference angle.

# Holographic photochemistry: developing, fixing and bleaching

