

Photographic Processing Hazards, by Michael McCann, Ph.D., CIH

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Black-and-White Photographic Processing

A wide variety of chemicals are used in black and white photographic processing. Film developing is usually done in closed canisters. Print processing uses tray processing, with successive developing baths, stop baths, fixing baths, and rinse steps. Other treatments include use of hardeners, intensifiers, reducers, toners, and hypo eliminators.

Mixing Photochemicals

Photochemicals can be bought in liquid form, which only need diluting, or powder form, which need dissolving and diluting.

Hazards

1. Developer solutions and powders are often highly alkaline, and glacial acetic acid, used in making the stop bath, is also corrosive by skin contact, inhalation and ingestion.
2. Developer powders are highly toxic by inhalation, and moderately toxic by skin contact, due to the alkali and developers themselves (see Developing Baths below).

Precautions

1. Use liquid chemistry whenever possible, rather than mixing developing powders. Pregnant women, in particular, should not be exposed to powdered developer.
2. When mixing powdered developers, use a glove box (a cardboard box with glass or plexiglas top, and two holes in the sides for hands and arms), local exhaust ventilation, or wear a NIOSH-approved toxic dust respirator.
3. Wear gloves, goggles and protective apron when mixing concentrated photochemicals. Always add any acid to water, never the reverse.
4. In case of skin contact, rinse with lots of water. In case of eye contact, rinse for at least 15 minutes, preferably using an eyewash station, seek medical attention.
5. Store concentrated acids and other corrosive chemicals on low shelves so as to reduce the chance of face or eye damage in case of breakage and splashing.

6. Do not store photographic solutions in glass containers.

Developing Baths

The most commonly used developers are hydroquinone, monomethyl para-amino phenol sulfate, and phenidone. Several other developers are used for special purposes. Other common components of developing baths include an accelerator, often sodium carbonate or borax, sodium sulfite as a preservative, and potassium bromide as a restrainer or antifogging agent.

Hazards

1. Developers are skin and eye irritants, and in many cases strong sensitizers. Monomethyl-p-aminophenol sulfate creates many skin problems, and allergies to it are frequent (although this is thought to be due to the presence of para-phenylene diamine as a contaminant). Hydroquinone can cause depigmentation and eye injury after five or more years of repeated exposure, and is a mutagen. Some developers also can be absorbed through the skin to cause severe poisoning (e.g., catechol, pyrogallol, pyrogallol acid). Phenidone is only slightly toxic by skin contact.
2. Most developers are moderately to highly toxic by ingestion, with ingestion of less than one tablespoon of compounds such as monomethyl-p-aminophenol sulfate, hydroquinone, or pyrocatechol being possibly fatal for adults. Symptoms include ringing in the ears (tinnitus), nausea, dizziness, muscular twitching, increased respiration, headache, cyanosis (turning blue from lack of oxygen due to methemoglobinemia, delirium, and coma). With some developers, convulsions also can occur.
3. Para-phenylene diamine and some of its derivatives are highly toxic by skin contact, inhalation, and ingestion. They cause very severe skin allergies and can be absorbed through the skin.
4. Sodium hydroxide, sodium carbonate, and other alkalis used as accelerators are highly corrosive by skin contact or ingestion. This is a particular problem with the pure alkali or with concentrated stock solutions.
5. Potassium bromide is moderately toxic by inhalation or ingestion and slightly toxic by skin contact. Symptoms of systemic poisoning include somnolence, depression, lack of coordination, mental confusion, hallucinations, and skin rashes.
6. Sodium sulfite is moderately toxic by ingestion or inhalation, causing gastric upset, colic, diarrhea, circulatory problems, and central nervous system depression. It is not appreciably toxic by skin contact. If heated or allowed to stand for a long time in water or acid, it decomposes to produce sulfur dioxide, which is highly irritating by inhalation.

Precautions

1. See the section on Mixing Photochemicals for mixing precautions.
2. Do not put your bare hands in developer baths. Use tongs instead. If developer solution splashes on your skin or eyes immediately rinse with lots of water. For eye splashes, continue rinsing for 15-20 minutes and seek medical attention.
3. Do not use para-phenylene diamine or its derivatives if at all possible.

Stop Baths and Fixer

Stop baths are usually weak solutions of acetic acid. Acetic acid is commonly available as pure glacial acetic acid or 28% acetic acid. Some stop baths contain potassium chrome alum as a hardener.

Fixing baths contain sodium thiosulfate ("hypo") as the fixing agent, and sodium sulfite and sodium bisulfite as a preservative. Fixing baths also may also contain alum (potassium aluminum sulfate) as a hardener and boric acid as a buffer.

Hazards

1. Acetic acid, in concentrated solutions, is highly toxic by inhalation, skin contact, and ingestion. It can cause dermatitis and ulcers, and can strongly irritate the mucous membranes. The final stop bath is only slightly hazardous by skin contact. Continual inhalation of acetic acid vapors, even from the stop bath, may cause chronic bronchitis.
2. Potassium chrome alum or chrome alum (potassium chromium sulfate) is moderately toxic by skin contact and inhalation, causing dermatitis and allergies.
3. In powder form, sodium thiosulfate is not significantly toxic by skin contact. By ingestion it has a purging effect on the bowels. Upon heating or long standing in solution, it can decompose to form highly toxic sulfur dioxide, which can cause chronic lung problems. Many asthmatics are particularly sensitive to sulfur dioxide.
4. Sodium bisulfite decomposes to form sulfur dioxide if the fixing bath contains boric acid, or if acetic acid is transferred to the fixing bath on the surface of the print.
5. Alum (potassium aluminum sulfate) is only slightly toxic. It may cause skin allergies or irritation.
6. Boric acid is moderately toxic by ingestion or inhalation and slightly toxic by skin contact (unless the skin is abraded or burned, in which case it can be highly toxic).

Precautions

1. All darkrooms require good ventilation to control the level of acetic acid vapors and sulfur dioxide gas produced in photography.
2. Wear gloves and goggles.
3. Cover all baths when not in use to prevent evaporation or release of toxic vapors and gases.

Intensifiers and Reducers

A common after-treatment of negatives (and occasionally prints) is either intensification or reduction. Common intensifiers include hydrochloric acid and potassium dichromate, or potassium chlorochromate. Mercuric chloride followed by ammonia or sodium sulfite, Monckhoven's intensifier consisting of a mercuric salt bleach followed by a silver nitrate/potassium cyanide solution, mercuric iodide/sodium sulfite, and uranium nitrate are older, now discarded, intensifiers.

Reduction of negatives is usually done with Farmer's reducer, consisting of potassium ferricyanide and hypo. Reduction has also been done historically with iodine/potassium cyanide, ammonium persulfate, and potassium permanganate/sulfuric acid.

Hazards

1. Potassium dichromate and potassium chlorochromate are probable human carcinogens, and can cause skin allergies and ulceration. Potassium chlorochromate can release highly toxic chlorine gas if heated or if acid is added.
2. Concentrated hydrochloric acid is corrosive; the diluted acid is a skin and eye irritant.
3. Mercury compounds are moderately toxic by skin contact and may be absorbed through the skin. They are also highly toxic by inhalation and extremely toxic by ingestion. Uranium intensifiers are radioactive, and are especially hazardous to the kidneys.
4. Sodium or potassium cyanide is extremely toxic by inhalation and ingestion, and moderately toxic by skin contact. Adding acid to cyanide forms extremely toxic hydrogen cyanide gas, which can be rapidly fatal.
5. Potassium ferricyanide, although only slightly toxic by itself, will release hydrogen cyanide gas if heated, if hot acid is added, or if exposed to strong ultraviolet light (e.g., carbon arcs). Cases of cyanide poisoning have occurred through treating Farmer's reducer with acid.
6. Potassium permanganate and ammonium persulfate are strong oxidizers and may cause fires or explosions in contact with solvents and other organic materials.

Precautions

1. Chromium intensifiers are probably the least toxic intensifiers, even though they are probable human carcinogens. Gloves and goggles should be worn when preparing and using these intensifiers. Mix the powders in a glove box or wear a NIOSH-approved toxic dust respirator. Do not expose potassium chlorochromate to acid or heat.
2. Do not use mercury, cyanide or uranium intensifiers, or cyanide reducers because of their high or extreme toxicity.
3. The safest reducer to use is Farmer's reducer. Do not expose Farmer's reducer to acid, ultraviolet light, or heat.

Toners

Toning a print usually involves replacement of silver by another metal, for example, gold, selenium, uranium, platinum, or iron. In some cases, the toning involves replacement of silver metal by brown silver sulfide, for example, in the various types of sulfide toners. A variety of other chemicals are also used in the toning solutions.

Hazards

1. Sulfides release highly toxic hydrogen sulfide gas during toning, or when treated with acid.
2. Selenium is a skin and eye irritant and can cause kidney damage. Treatment of selenium salts with acid may release highly toxic hydrogen

selenide gas. Selenium toners also give off large amounts of sulfur dioxide gas.

3. Gold and platinum salts are strong sensitizers and can produce allergic skin reactions and asthma, particularly in fair-haired people.
4. Thiourea is a probable human carcinogen since it causes cancer in animals.

Precautions

1. Carry out normal precautions for handling toxic chemicals as described in previous sections. In particular, wear gloves and goggles. See also the section on Mixing Photochemicals.
2. Toning solutions must be used with local exhaust ventilation.
3. Take precautions to make sure that sulfide or selenium toners are not contaminated with acids. For example, with two bath sulfide toners, make sure you rinse the print well after bleaching in acid solution before dipping it in the sulfide developer.
4. Avoid thiourea whenever possible because of its probable cancer status.

Other Hazards

Many other chemicals are also used in black and white processing, including formaldehyde as a pre-hardener, a variety of oxidizing agents as hypo eliminators (e.g., hydrogen peroxide and ammonia, potassium permanganate, bleaches, and potassium persulfate), sodium sulfide to test for residual silver, silver nitrate to test for residual hypo, solvents such as methyl chloroform and freons for film and print cleaning, and concentrated acids to clean trays.

Electrical outlets and equipment can present electrical hazards in darkrooms due to the risk of splashing water.

Hazards

1. Concentrated sulfuric acid, mixed with potassium permanganate or potassium dichromate, produces highly corrosive permanganic and chromic acids.
2. Hypochlorite bleaches can release highly toxic chlorine gas when acid is added, or if heated.
3. Potassium persulfate and other oxidizing agents used as hypo eliminators may cause fires when in contact with easily oxidizable materials, such as many solvents and other combustible materials. Most are also skin and eye irritants.

Precautions

1. See previous sections for precautions in handling photographic chemicals.
2. Cleaning acids should be handled with great care. Wear gloves, goggles and acid-proof, protective apron. Always add acid to the water when diluting.
3. Do not add acid to, or heat, hypochlorite bleaches.
4. Keep potassium persulfate and other strong oxidizing agents separate from flammable and easily oxidizable substances.

5. Install ground fault interrupters ([GFCIs](#)) whenever electrical outlets or electrical equipment (e.g. enlargers) are within six feet of the risk of water splashes.

Color Processing

Color processing is much more complicated than black and white processing, and there is a wide variation in processes used by different companies. Color processing can be either done in trays or in automatic processors.

Developing Baths

The first developer of color transparency processing usually contains monomethyl-p-aminophenol sulfate, hydroquinone, and other normal black and white developer components. Color developers contain a wide variety of chemicals including color coupling agents, penetrating solvents (such as benzyl alcohol, ethylene glycol, and ethoxydiglycol), amines, and others.

Hazards

1. See the developing section of black and white processing for the hazards of standard black and white developers.
2. In general, color developers are more hazardous than black and white developers. Para-phenylene diamine, and its dimethyl and diethyl derivatives are known to be highly toxic by skin contact and absorption, inhalation, and ingestion. They can cause very severe skin irritation, allergies and poisoning. Color developers have also been linked to lichen planus, an inflammatory skin disease characterized by reddish pimples which can spread to form rough scaly patches. Recent color developing agents such as 4-amino-N-ethyl-N-[P-methane- sulfonamidoethyl]-m-toluidine sesquisulfate monohydrate and 4-amino-3-methyl-N-ethyl-N-[3-hydroxyethyl]-aniline sulfate are supposedly less hazardous, but still can cause skin irritation and allergies.
3. Most amines, including ethylene diamine, tertiary-butylamine borane, the various ethanolamines, etc., are strong sensitizers, as well as skin and respiratory irritants.
4. Although many of the solvents are not very volatile at room temperature, the elevated temperatures used in color processing can increase the amount of solvent vapors in the air. The solvents are usually skin and eye irritants.

Precautions

1. Wear gloves and goggles when handling color developers. Wash gloves with an acid-type hand cleaner (e.g. pHisoderm (R)), and then water before removing them.
2. Mix powders in a glove box, or wear a NIOSH-approved toxic dust respirator.
3. Color processing needs more ventilation than black and white processing due to the use of solvents and other toxic components at elevated temperatures.

Bleaching, Fixing, and Other Steps

Many of the chemicals used in other steps of color processing are essentially the same as those used for black and white processing. Examples include the stop bath and fixing bath. Bleaching uses a number of chemicals, including potassium ferricyanide, potassium bromide, ammonium thiocyanate, and acids. Chemicals found in prehardeners and stabilizers include succinaldehyde and formaldehyde; neutralizers can contain hydroxylamine sulfate, acetic acid, and other acids.

Hazards

1. Formaldehyde is moderately toxic by skin contact, and highly toxic by inhalation and ingestion. It is a skin, eye and respiratory irritant, and strong sensitizer, and is a probable human carcinogen. Formaldehyde solutions contain some methanol, which is highly toxic by ingestion.
2. Succinaldehyde is similar in toxicity to formaldehyde, but is not a strong sensitizer or carcinogen.
3. Hydroxylamine sulfate is a suspected teratogen in humans since it is a teratogen (causes birth defects) in animals. It is also a skin and eye irritant.
4. Concentrated acids, such as glacial acetic acid, hydrobromic acid, sulfamic acid and p-toluenesulfonic acids are corrosive by skin contact, inhalation and ingestion.
5. Acid solutions, if they contain sulfites or bisulfites (e.g., neutralizing solutions), can release sulfur dioxide upon standing. If acid is carried over on the negative or transparency from one step to another step containing sulfites or bisulfites, then sulfur dioxide can be formed.
6. Potassium ferricyanide will release hydrogen cyanide gas if heated, if hot acid is added, or if exposed to strong ultraviolet radiation.

Precautions

1. Local exhaust ventilation is required for mixing of chemicals and color processing.
2. Use premixed solutions whenever possible.
3. Avoid color processes using formaldehyde, if possible.
4. Wear gloves, goggles and protective apron when mixing and handling color processing chemicals. When diluting solutions containing concentrated acids, always add the acid to the water. An eyewash should be available.
5. A water rinse step is recommended between acid bleach steps and fixing steps to reduce the production of sulfur dioxide gas.
6. Do not add acid to solutions containing potassium ferricyanide or thiocyanate salts.
7. Control the temperature carefully according to manufacturer's recommendations to reduce emissions of toxic gases and vapors.